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Proceedings of the Joint Symposium on Stationary Combustion NO_x Control

Volume IV

NO_x Control and Environmental Assessment of Industrial Process Equipment, Engines, and Small Stationary Sources

Symposium Cochairmen
Robert E. Hall, EPA
and
J. Edward Cichanowicz, EPRI

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16. ABSTRACT

The proceedings document the approximately 50 presentations made during the symposium, October 6-9, 1980, in Denver, CO. The symposium was sponsored by the Combustion Research Branch of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, and the Electric Power Research Institute (EPRI), Palo Alto, CA. Main topics included utility boiler field tests; NOx flue gas treatment; advanced combustion processes; environmental assessments; industrial, commercial, and residential combustion sources; and fundamental combustion research. This volume relates to NOx control and environmental assessment of industrial process equipment, engines, and small stationary sources.

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Nitrogen Oxides		Environmental Assessment	07B	
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PREFACE

These proceedings document more than 50 presentations given at the Joint Symposium on Stationary Combustion NO_x Control held October 6-9, 1980 at the Stouffer's Denver Inn in Denver, Colorado. The symposium was sponsored by the Combustion Research Branch of the EPA's Industrial Environmental Research Laboratory-Research Triangle Park and the Electric Power Research Institute (EPRI). The presentations emphasized recent developments in NO_x control technology. Cochairmen of the symposium were Robert E. Hall, EPA, and J. Edward Cichanowicz, EPRI. Introductory remarks were made by Dan V. Giovanni, Program Manager for Air Quality Control, Coal Combustion Systems Division, EPRI, and the welcoming address was given by Roger L. Williams, Regional Administrator, EPA Region VIII. Stephen J. Gage, Assistant Administrator for Research and Development, EPA, was the keynote speaker. The symposium had 11 sessions:

I: NO_x Emissions Issues
Michael J. Miller, EPRI, Session Chairman

II: Manufacturers Update of Commercially Available Combustion Technology
Joshua S. Bowen, EPA, Session Chairman

III: NO_x Emissions Characterization of Full Scale Utility Powerplants
David G. Lachapelle, EPA, Session Chairman

IV: Low NO_x Combustion Development
Michael W. McElroy, EPRI, Session Chairman

Va: Postcombustion NO_x Control
George P. Green, Public Service Company of Colorado, Session Chairman

Vb: Fundamental Combustion Research
Tom W. Lester, EPA, Session Chairman

VI: Status of Flue Gas Treatment for Coal-Fired Boilers
Dan V. Giovanni, EPRI, Session Chairman

VII: Large Industrial Boilers
J. David Mobley, EPA, Session Chairman

VIII: Small Industrial, Commercial, and Residential Systems
J. David Mobley, EPA, Session Chairman

IX: Environmental Assessment
Robert P. Hangebrauck, EPA, Session Chairman

X: Stationary Engines and Industrial Process Combustion Systems
Robert E. Hall, EPA, Session Chairman

XI: Advanced Processes
G. Blair Martin, EPA, Session Chairman

VOLUME IV

TABLE OF CONTENTS

Page

Session VII: Small Industrial, Commercial, and Residential Systems

"Evaluation of Emissions and Control Technology for Industrial Stoker Boilers," R. D. Giammar, R. H. Barnes, D. R. Hopper, P. R. Webb, and A. E. Weller 1

"Control of Emissions from Residential Wood Combustion by Combustion Modification," J. M. Allen 39

"Field Tests of Eleven Stoker Coal-Fired Boilers for Emissions Control and Improved Efficiency," P. L. Langsjoen 64

Session VIII: Large Industrial Boilers

"Combustion Modification for Coal-Fired Stoker Boilers," K. L. Maloney, K. F. Maloney, and M. J. Pfefferle 83

"Thirty-Day Field Tests of Industrial Boiler Combustion Modifications," W. A. Carter 99

"Applicability of Thermal DeNO$_x$ to Large Industrial Boilers," B. E. Hurst and C. E. Schleckser, Jr. 118

Session IX: Environmental Assessment

"Conventional Combustion Environmental Assessment Program," W. H. Ponder 148

"Combustion Modification Environmental Assessment," C. Castaldini, R. M. Evans, E. B. Higginbotham, K. J. Lim, H. B. Mason, and L. R. Waterland 177

"Utility Boiler Environmental Assessment - The EPRI Approach," M. W. Zengerle 218

Page

Session X: Stationary Engines and Industrial Process Combustion Systems

"Characterization and Oxidation of Diesel Particulate," D. A. Trayser, L. J. Hillenbrand, M. J. Murphy, J. R. Longanbach, and A. Levy 233

"Single Cylinder Tests of Emission Control Methods for Large-Bore Stationary Engines," R. P. Wilson, Jr. 270

"Emission Reduction by Combustion Modification for Petroleum Process Heaters," R. J. Tidona, W. A. Carter, J. R. Hart and S. C. Hunter 320

"Kinetics and Mixing in Industrial Afterburners," A. Levy, A. A. Putnam, H. A. Arbib, and R. H. Barnes 347

"Subscale Tests of Combustion Modification for Steel Furnaces," R. J. Tidona, W. A. Carter, and S. C. Hunter . . . 396

EVALUATION OF EMISSIONS AND CONTROL TECHNOLOGY FOR INDUSTRIAL STOKER BOILERS

By:

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ABSTRACT

This paper presents the results of a 3-phase program to evaluate emissions and control technology for industrial stoker boilers. The paper focuses on the third phase "Limestone/Coal Pellet Development", while summaries are given of the first two phases, "Alternate Fuels Evaluation" and "Control Technology Evaluation". Because SO_2 appears to be the most troublesome emission to control for stokers, a limestone/high sulfur coal pellet was developed and evaluated as a SO_2 control technique. Initially, this pellet with a Ca/S molar ratio of 7 was successfully fired in a 8 MW_{th} industrial spreader-stoker boiler with SO_2 emissions reduced by 75 percent. However, from both an economical and operational standpoint, the amount of limestone required had to be reduced to correspond to Ca/S molar ratio of 3 to 4. Furthermore, the mechanical properties of this pellet were inadequate to withstand the severe stresses of an industrial fuel-handling system. Accordingly, an R&D effort was undertaken to refine the pellet. A refined pellet, with a Ca/S molar ratio of 3-1/2 with appropriate binders was produced that had similar or improved physical characteristics of raw coals. Additionally, economic analysis indicates that this pellet can be produced for approximately $15/ton above the cost of the high sulfur coal. This refined pellet was fired in a 200 kW_{th} laboratory spreader-stoker boiler achieving sulfur captures as high as 70 percent. However, when fired in the 8 MW_{th} (25,000 lb steam/hr) stoker boiler, sulfur captures on the order of 50 percent were achieved.

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We would also like to acknowledge Harold Johnson of Detroit Stoker, William Engelleitner of Mars-Mineral, Sam Spector of Banner Industries, and Donald Hansen of Alley-Cassetty Coal Company for providing advice and assistance to the program.

Finally, we would like to recognize Battelle-Columbus staff members--John Faught, Tom Lyons, Paul Strup, Don Hupp, Luis Kahn, and Andrew Skidmore, and acknowledge the cooperation of John Clayton and his Facilities staff who allowed us to use the Battelle steam plant boiler during the program.

SECTION I

INTRODUCTION

The coal-fired stoker boiler provides an option for industry to meet its energy needs. This option has not been exercised by a significant number of industries primarily because oil- and gas-fired equipment have been, and still are, more environmentally and economically attractive. However, with the dwindling supplies of oil and gas, the rising costs of these fuels, and increased attention given to coal utilization, industry once again is considering the coal-fired stoker boiler.

In support of our nation's commitments to maintain a clean environment and to utilize coal, EPA funded a research and development program to identify and demonstrate improvements in stoker-coal firing that can provide an incentive for greater industrial use of coal. The overall objectives of this program were to

- Characterize the spectrum of emissions from industrial coal-fired stoker boilers using several types of coal under various stoker-firing conditions
- Investigate control methods to reduce these emissions
- Determine the effect of these control methods and variations in stoker-boiler operation on the overall performance of the stoker boiler, and,
- Assess the environmental impact of new technology on the future acceptability of stoker boilers.

This program was recently completed and the final report should be available soon.

This program was divided into three phases. In Phase I, Alternative Fuels Evaluation, emission characteristics were determined for a variety of coals fired in a 200-kW_t stoker boiler. Emphasis was focused on identifying coals with low pollutant potential, including both physically and chemically treated coals. The results of this phase were presented at the Second Stationary Source Combustion Symposium and contained in its Proceedings. In Phase II, Control Technology Evaluation, potential concepts for control of emissions for full-scale industrial stokers were evaluated. Similarly the results of this phase were presented at the Third Stationary Source Combustion Symposium and contained in its Proceedings. In Phase III, Limestone/Coal Pellet Development, a limestone/coal fuel pellet was developed and evaluated as to its viability as an SO_2 control for industrial stoker boilers. This paper focuses on that effort and summarizes those results. The executive summaries of Phases I and II of the final report of this program are also included in this paper.

SECTION II

PHASE I. ALTERNATE FUELS EVALUATION

EXECUTIVE SUMMARY

A 200-kW stoker-boiler facility was used to evaluate characteristics of emissions from combustion of a variety of coals, including coals that could not be conveniently or economically evaluated in larger industrial systems. The stoker was initially operated in an underfeed mode to expand the data base developed in an earlier EPA program (1). This facility was modified to accommodate a model spreader stoker more typical of an industrial boiler.

Raw coals with low pollution potential and treated coals were evaluated. Because there was only one treated coal available during the time framework of the program, Battelle developed, as part of this program, a limestone/high sulfur coal fuel pellet.

Results of the Phase I emission characterization were as follows.

NO

For the underfeed stoker, less than 10 percent of the fuel nitrogen was converted to NO, assuming no thermal NO. For the model spreader-stoker, between 10 and 20 percent of the fuel nitrogen was converted to NO.

SO_2

Coals naturally high in calcium and sodium and those treated with these elements retained significant percentages of the sulfur in the ash. For the eastern bituminous coals, with relatively small amounts of calcium and sodium but significant amounts of iron, sulfur retention in the ash was as high as 20 percent. It was observed that bed temperatures in these laboratory stokers are significantly lower than those measured in an industrial stoker.

CO

CO levels can be controlled by the use of overfire air and were generally less than 100 ppm.

Particulate Loading

Particulate loadings did not correlate consistently with either the ash content of the coal nor its size consist prior to feeding. It appears that the friability and inherent moisture content of the coal may affect particulate loading since these properties influence the amount of fines generated.

POM Loadings

POM loadings for continuous operation of the underfeed stoker were significantly less than those reported earlier (1) for intermittent operation.

Particle-Size Distribution

For the model spreader, the average stack particle size ranged between 15 and 30 micrometers.

Treated Coals

No commercially available, chemically treated coals were identified. Treated coals required pelletization for firing in stokers.

The Battelle Hydrothermally Treated (HTT) coal was available for laboratory evaluation. The treatment reduced the fuel sulfur from 2.6 percent to 1.1 percent. Because of the relatively high calcium and sodium residual from the treatment, only 28 percent of the remaining sulfur was emitted as SO_2.

Also, the limestone/coal fuel pellet, with a Ca/S molar ratio of 7, reduced SO_2 emissions by over 70 percent. Even at the elevated fuel-bed temperatures (> 1100 C), the calcium reacts with the coal sulfur and retains it as a sulfide/sulfate as part of the fuel ash.

SECTION III

PHASE II. CONTROL TECHNOLOGY EVALUATION

EXECUTIVE SUMMARY

Potential control concepts were identified and evaluated in the Battelle 8 MW_{th} (25,000 lb steam/hr) spreader stoker boiler. Control strategies were limited to:

- Use of compliance coals
- Combustion-system operational modifications
- Minor combustion-system design modification
- Use of treated coal (limestone/coal fuel pellet).

Flue-gas clean-up techniques were not considered. Criteria pollutants were used as the basis for evaluation.

The Phase II experiments have demonstrated that emission levels can be reduced by proper control of the stoker operating variables. In addition, the limestone/coal pellets have been demonstrated to offer potential for SO_2 control. In summary, the major findings are:

- The limestone/high-sulfur coal pellet showed a sulfur capture of about 75 percent for a Ca/S molar ratio of 7.
- Sulfur capture efficiencies of around 25 percent were noticed with some eastern bituminous coals.
- High excess air rates at low loads resulted in increased sulfur retention in the bed ash.
- CO and smoke levels were controlled by providing adequate excess air. CO levels were low for all fuels tested, except the limestone/coal fuel pellet.
- Clinker formation may be a limiting factor in determining the minimum excess air rate.
- NO levels increased slightly with increased excess air.

- An increase in overfire air/total air flow rate ratio reduced CO and smoke, the latter more significantly. Particulate loadings were also reduced with increased overfire air.
- NO was lower for inactive overfire air jets
- Clinker formation occurred readily if bed depths became excessive, while the danger of burning the grates existed for operation with very shallow beds. Bed depths around 6.3 to 7.6 cm appeared to be optimum for lower ash coals.
- POM levels ranged from 13 to 24 $\mu g/Nm^3$. They were somewhat lower than those of the model spreader and only slightly higher than those from a 500 kW_{th} packaged boiler firing natural gas and fuel oil (2).
- A higher excess air rate was required for low-load than for partial- or full-load operation. Additionally, a greater percentage of overfire air was required at low load. Low-load smoke can be reduced by a reduction in underfire air, coupled with attentive boiler operation.
- At full load fly-ash reinjection increase boiler efficiency by 1.5 percent. However, particulate loadings were reduced by 10 to 25 percent by operating without fly-ash reinjection.
- The high-sulfur Ohio coals had to be fired at higher excess air rates than did the low-sulfur Ohio and Kentucky coals. The high-ash unwashed stoker coal and high-moisture Illinois No. 6 coal could not be fired satisfactorily.
- Improvements in the coal feed system will increase control of fuel distribution within the stoker boiler and thus offer an improved control of the combustion process. Coal particle segragation by the transport system was significant in the 8 MW_{th} stoker boiler.
- Improved grate design to minimize leakage and to provide more uniform air distribution would also improve the control of combustion process and reduce emissions and increase boiler efficiency.
- Improved overfire air systems to increase the effectiveness of aerodynamic mixing above the bed is one of the more promising combustion modification techniques to reduce emissions and improve performance.

SECTION IV

PHASE III. LIMESTONE/COAL PELLET DEVELOPMENT

EXECUTIVE SUMMARY

The Phase III program focused on refinement of the limestone/coal fuel pellet and evaluation of its suitability as an industrial stoker-boiler fuel. This program consisted of four major tasks:

1. Pellet Development aimed at developing a fuel pellet with mechanical strength characteristics that can withstand weathering and the severe stresses of an industrial stoker coal-handling and feeding system, burns at reasonable rates, and captures sufficient sulfur to be competitive with other control strategies. Mechanical strength characteristics were evaluated with standard laboratory tests. Burning characteristics and sulfur capture were determined in a fixed-bed reactor simulating the fuel bed of a spreader stoker.

2. Process Variables Selection combined a mathematical model analysis with a series of experimental studies to develop a more comprehensive understanding of the processes that influence the combustion of the fuel pellet and control the capture of sulfur.

3. Laboratory Evaluations conducted in both the 200 kW_t model-spreader stoker and the 8 MW_t Battelle steam plant boiler to evaluate the most promising candidate pellets.

4. Economic Analysis aimed at developing pellet process costs.

The major results and conclusions of the four tasks are:

Pellet Development

- A fuel pellet was produced that, according to laboratory tests, has mechanical strength and durability characteristics similar to those of conventional coals.
- Pellets produced by auger extrusion or pellet mill processes had better mechanical strength than those produced by disc pelleting or briquetting.
- Binders that provide some resistance to the weather were identified. However, no binder was identified that provided complete weather proofing.
- The fixed-bed reactor experiments indicated a weak dependency between Ca/S ratio and sulfur capture for Ca/S ratios above 2.
- Calcium oxide is a superior absorbent to limestone, but is not economically competitive with limestone.
- Additives do not appear to enhance sulfur capture.

Process Variables Selection

- The mathematical model predicts an optimum coal size (35-40 mm diameter) for maximum sulfur retention.
- The model indicates a weak dependency on the calcium/sulfur ratio.
- Scanning electron microscopy and x-ray diffusion are powerful tools for the study of solid-state reactions in the pellets. Results indicate that sulfur is retained predominantly as $CaSO_4$.
- Sulfur may react directly with limestone by solid-state processes without involving the formation of SO_2.

Laboratory Evaluations

- Auger-extruded and milled pellets burned better than briquets and disc-agglomerated pellets.
- Sulfur capture of about 65 percent was achieved at Ca/S molar ratios of 3.5.

- Sulfur capture of about 50 percent was achieved in the steam-plant stoker. In comparison to the model spreader, this lower SO_2 capture was attributed to higher temperatures (in excess of 1300 C).

- In the Battelle steam power plant, the fuel pellets burned as well as low-sulfur coal.

Economic Analysis

- It is estimated that limestone/coal fuel pellets can be produced for about $15.40/Mg ($14/ton) of pellets above the costs of the high-sulfur coal.

SECTION V

BACKGROUND

During Phase II of this program, Control Technology Evaluation, SO_2 was considered as the most troublesome emission to control in an industrial stoker-boiler system. The other criteria emissions could be controlled with existing technology or were within the current emissions requirements. As a result, and because the limestone/coal fuel pellet offers a means for environmentally acceptable burning of high-sulfur coal in existing boilers, EPA continued the development of the fuel pellet as part of this program.

From an industrial point of view, the possibilities of using limestone/coal pellets for removing SO_2 in situ via a dry process is more acceptable than the use of scrubbers. The additional costs for pelletizing the coal/limestone mixture and for the removal of 3 to 4 times as much ash is far more attractive than the high cost of operating and maintaining wet scrubbers.

SECTION VI

PELLET DEVELOPMENT

The fuel pellets used in earlier studies did not have adequate strength or durability as up to 50 percent fines were introduced into the $8MW_{th}$ (25,000 lb steam/hr) boiler. Furthermore, from both an economical and operational standpoint, the amount of limestone required to capture a target goal of 70 percent fuel sulfur had to be reduced to correspond to a Ca/S molar ratio of 3 to 4. As a result, an extensive effort (166 test samples) was made to investigate:

- pellet production techniques
- binder types
- coal and limestone particle sites
- limestone types
- pellet formulations.

Laboratory test procedures were developed to evaluate the effect of these variables on the mechanical strength properties of the fuel pellets.

Illinois No. 6 coal was used as the base coal. This coal was ground to 100 percent through 20-mesh and 50 percent through 100-mesh. Ground limestone (-50 mesh) was added to the coal with the selected binders and thoroughly mixed. This mixture was fed to a pellet mill to produce cylindrical pellets one-half inch in diameter and about three-fourth inch long.

Table I indicates that pellets were produced with mechanical strength, durability and weatherability characteristics similar to those of raw coals based upon the laboratory test procedures. A number of formulations were identified that could produce satisfactory pellets. The specific formulation used will depend on economics and availability.

The reader is referred to the final report for detailed discussion.

SECTION VII

PROCESS VARIABLES SELECTION

A mathematical modeling analysis, in combination with a series of experimental studies, was performed to develop a more comprehensive understanding of the processes that influence the burning of the coal/limestone pellets and control sulfur capture. The purpose of the experimental studies was to provide physical and chemical rate constants for the model, and to provide a basis for assessing model reliability. The main objectives of the modeling studies were to predict burning rates and sulfur capture as a function of pellet properties such as size, composition, and physical structure under different combustion conditions. Knowledge of how these parameters affect pellet performance is important for the development of optimum pellets for specific boiler applications.

The mathematical model described here is a preliminary model with a number of simplifying assumptions incorporated into it. An important purpose of this effort was to demonstrate how modeling can be practically and usefully employed to understand how coal/limestone pellets behave and how to improve their performance. The basic structure of this preliminary model can be expanded to include either additional processes or refined mechanisms to increase its accuracy.

In the model, the pellet's cylindrical geometry is represented by an equivalent sphere having the same surface-to-volume ratio. The burning of the pellet is represented by the shrinking core model developed bv Wen and co-workers (3-6). It is based on a burning reaction zone that penetrates into the pellet and is supported by oxygen that diffuses through the ash layer surrounding the burning core. SO_2, formed at the burning interface between the unburned core and ash, is assumed to diffuse out through the ash layer where it is captured by the $CaCO_3$ in the limestone. The calcination process is represented by the reaction

$$CaCO_3 \rightarrow CaO + CO_2$$

and sulfur capture by the reaction

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 \quad .$$

SO_2 that does not react with the CaO while diffusing to the outer surface of the ash layer is considered to be released from the pellet. The model, in its present form, neglects factors such as heat transfer, devolatilization of the coal, the reaction between CO_2 and carbon forming CO, and solid-state reactions. These mechanisms can be incorporated into extended versions of the present model as appropriate.

The experimental studies associated with the modeling effort were performed using the fixed-bed reactor described in detail in the final report. These experiments involved heating pellets in the fixed-bed reactor in a flowing air stream for various periods of time corresponding to different levels of fuel consumption in the pellets. The combustion gases exiting from the reactor were analyzed continuously for SO_2, CO, and O_2 to follow the kinetic rates of the combustion and SO_2-release processes. Burned pellets were recovered, weighed, analyzed chemically, and subjected to examination by metallographic techniques, scanning electron microscopy, and X-ray diffraction. Some limitations, however, exist in accurately applying some of these data to the model because of uncertainties in the fixed-bed reactor experiments. These difficulties can be eliminated in future work by using the model developed here as a guide for designing the experiments.

The results of this effort are summarized in the Executive Summary. Further details on both the fixed-bed reactor experiments and the model are presented in the final report.

SECTION VIII

LABORATORY EVALUATION

The promising pellet formulations identified during the mechanical strength and fixed-bed reactor experiments were evaluated in the model spreader-stoker boiler. This evaluation was based on gaseous emissions (primarily SO_2) and visual observations of the fuel bed. In addition, 18 Mg of the most promising pellet formulation were fired in the Battelle steamplant stoker. Criteria pollutants, visual observations, and ash analyses were used in these evaluations. Both facilities have been described in earlier symposium proceedings.

MODEL SPREADER EXPERIMENTS

To supplement the fixed-bed reactor experiments, the model spreader-stoker boiler was used to evaluate the more promising pellet formulations. Compared to the fixed-bed reactor, the model spreader provides an improved simulation of the operation of an industrial stoker boiler and thus evaluates the fuel pellet more realistically.

Table II presents the results of these experiments. In these experiments, the effect of Ca/S ratio (3.5 and 7), the four pellet production techniques, and binder type (cement and methylcellulose) were investigated. Additionally, for comparison, experiments were conducted with medium-S Kentucky coal, Illinois No. 6 coal, and the 50/50 pellets produced during Phase II. Prior to experimentation, the sampling system and procedures were modified to minimize any reactions that may occur in the sampling system.

Sampling System

The sampling system was a modification of that used during the Phase II experiments. An in-stack filter was used upstream of the water trap and the water trap was coupled as close to the stack as physically possible.

Modifications were made to minimize the presence of water (especially water with calcium-laden particulates) in the sampling system that could remove SO_2. Provisions were also made to span the instruments by injecting calibration gases through the entire sampling system before, during, and after the experiments. This procedure indicated no loss of SO_2 in the sampling train at any time during the experiment.

A comparison of the model-spreader pellet data from the Phase III experiments with those from Phase I indicate that sulfur capture was not as great (about 10 to 15 percent lower) for the Phase III experiments. This small reduction may be attributed to the improved sampling system where precautions were taken to minimize sulfur capture in the sampling line. Because of the difficulty in obtaining a representative sample, sulfur retention based on SO_2 emission levels could not be verified from a sulfur analysis of the bed ash.

Ca/S Ratio

The fixed-bed reactor experiments indicated that the Ca/S ratio had little or no effect on sulfur capture for Ca/S ratios greater than 3.5. The model spreader data presented in Table II confirm this observation. Visual observations indicated, as expected, that the pellets with less limestone (Ca/S = 3.5) burned more uniformly and rapidly than those with more limestone (Ca/S = 7).

Production Technique

Pellets using the same formulation consisting of Illinois No. 6 coal, limestone (Ca/S = 3.5), and methylcellulose binder, were prepared by the following production techniques:

- Pellet mill (prepared by Battelle staff)
- Auger extrusion (prepared by Banner Industries)
- Disc agglomeration (prepared by Mars Mineral Corporation)
- Briquets (prepared by Evergreen Company).

The pellet-mill and auger-extruded pellets burned satisfactorily, having sulfur captures of 67 and 63 percent, respectively. The auger extruded pellets were observed to burn more uniformly than the pellet mill pellets perhaps because they were more porous (~1.0 g/cc compared to ~1.4 g/cc).

The briquetted formulations showed relatively low sulfur retention (52 percent) -- a surprising and unexplained result. These pellets burned satisfactorily. The disc agglomerated pellets were entirely unsatisfactory when fired in the model spreader. These pellets disintegrated in the combustion zone producing excessive amounts (greater than 50 percent) of fines. Such fines matted the bed causing nonuniform air distribution. Fuel-bed conditions degraded so rapidly that meaningful data could not be obtained.

Binder Type

Comparison of sulfur retention data of the auger-extruded and mill-pellets made with organic (methylcellulose) and inorganic (cement) binders indicated no significant difference. The binders are used in very small quantities (less than 4 percent) and do not have any catalytic effects. As a result, it appears that the type of binder does not significantly effect the combustion behavior of the pellet providing the physical properties of the pellet are retained. Cement-bound pellets with satisfactory physical properties could not be made by the disc agglomeration and briquetting methods.

STEAMPLANT STOKER DEMONSTRATION

Eighteen Mg of the limestone coal fuel pellets with a Ca/S molal ratio of approximately 3.5 were fired in the steamplant boiler. Two types of pellets were used -- a lower density (0.9 to 1.2 g/cc) pellet produced by Banner Industries using sugar extrusion and a higher density pellet ($\approx$ 1.4 g/cc) produced by Alley-Cassetty Coal Company using a pellet mill. Both types of pellets were fired under a variety of boiler conditions. Evaluations were based on visual observations, criteria pollutants, and ash analyses.

PELLET PROPERTIES

Allbond-200 cornstarch and M-167 latex emulsion were used as binders. The resulting pellet formulation (dry basis) consisted of:

67 percent Illinois No. 6 coal
30 percent Piqua limestone
2 percent Allbond 200 binder
1 percent M-167 latex binder.

These pellets were cylindrical, about 13-mm in diameter and 25- to 75-mm long. Table III gives the proximate and ultimate analyses and also the ash-fusion temperature (initial deformation) for these pellets. Table IV gives the mineral analysis of the ash.

The high CaO in the ash of the treated coal preclude the usual procedures for evaluating ash characteristics, which are limited to about 20 percent CaO. The excess CaO above that which will react with the other ash constituents, principally with SiO_2, to form a low-viscosity slag, provides a matrix of solid CaO particles. Thus, in the ASTM cone fusion determination, this matrix retains the original shape of the cone, probably even at temperatures above 1650 C, which explains the anomalous data on the "fusion temperature" of the ash.

The high CaO content physically interferes with flow of the fluid slag that would result with a smaller addition of CaO. For example, if the CaO content of typical Illinois No. 6 coal ash were increased to only 20 percent on a normalized basis, the resulting fluxed coal ash would have a viscosity of only 10 poise at 1430 C, comparable to that of castor oil at room temperature. With 60.7 percent CaO, the ash will behave as a solid rather than a liquid because of all the unreacted CaO.

The pellets remained sufficiently intact during storage and handling that an acceptable pellet was fed into the boiler. However, it was observed that some pellets softened during exposure to rain. Weatherability tests on these pellets were rerun showing approximately the same characteristics. It appears that the weatherability test used during pellet development has some limitations and that pellets will require some undercover storage or further formulation refinement for weatherproofing.

EXPERIMENTAL RESULTS

Checkout Runs

Prior to the demonstration test, the fuel pellets were fired for 10 hours to determine the necessary stoker adjustments and to establish a range of operating conditions.

The limestone/coal pellets were fired without any adjustment to the stoker mechanism, previously set for a low-sulfur Ohio stoker coal. The stoker feed mechanism distributed the pellets uniformly over the grate. This was unexpected since the pellets were all approximately the same size. It was observed, however, that approximately 50 percent of the pellets broke randomly into smaller pieces providing a reasonably good size distribution.

a. Phase II/Phase III Pellet Comparison. Pellets fired in the Phase III study were significantly superior to those fired in the Phase II steamplant runs. They burned more readily at lower excess air rates, provided improved boiler response (thinner bed), ignited more readily, and generated lower CO and smoke levels. These improvements are attributed to the fact that the Phase III fuel had a higher heating value, contained an organic (rather than inorganic binder), contained less ash, and exhibited superior mechanical strength. However, sulfur retention was not as high with the Phase III pellets.

b. Stoker Coal/Phase III Pellet Comparison. Phase III pellets appeared to burn equally as well as the low-sulfur Ohio coal that is normally fired in the Battelle steamplant boiler. The boiler appeared to be as responsive to the load and could be operated at comparable excess air levels. Table V compares these two fuels. Emissions are corrected to 3 percent O_2.

c. Effect of Operating Parameters on Sulfur Retention. Because it was not the intent of the checkout runs to characterize the emissions for a variety of boiler operating conditions nor was it possible with the limited supply of fuel pellets, only limited amounts of data were collected in the checkout runs.

Sulfur retention was observed to decrease for increasing load as indicated below for relatively constant excess air (about 80 percent).

Boiler Load, percent full load	Sulfur Retention, percent	Bed Temperature, C
0.64	50	1315
0.80	48	1405
0.85	47	1425

The bed temperatures were measured with an optical pyrometer sighted on the combustion zone at the top surface of the bed. Sulfur retention varies with bed temperature. However, this observation must be tempered as the combustion conditions were not closely controlled throughout these and the observed temperature measurement may not be a good indication of the actual bed temperature.

At a low-load condition, the excess O_2 was varied from 9.5 percent to 16 percent with no significant change in the SO_2 retention (46 to 50 percent). Bed depths were also varied from 80 to 160 mm. SO_2 retention increased somewhat with deeper beds. The increased retention was attributed to the lower bed temperatures measured for the deeper beds.

Demonstration Test

During the limestone/coal fuel pellet demonstration, the pellet feed rate was maintained at approximately 1360 Kg/hr for a boiler load of 80 percent. Tables VI, VII, VIII, and IX summarize the results of this test.

a. Sulfur Capture. As indicated in Table VI, sulfur capture was 45 percent during the demonstration test. This sulfur retention is less than that observed for the model spreader and fixed-bed reactor experiments firing pellets of similar formulations. Additionally, as previously discussed, a 75 percent sulfur retention was achieved when firing a cement-bound pellet with a Ca/S ratio of 7 in the steamplant during Phase II. The greater sulfur retention of these other experiments is attributed to the lower bed temperatures, which seldom exceeded 1260 C. The bed temperatures in the Phase III steamplant demonstration were seldom less than 1370 C and ran as high as 1455 C. Additionally, with a pulsating ash discharge stoker, the fuel bed is violently disturbed. Ash can be recirculated back into the hot zone. Thus, if sulfur is retained in the ash at a lower bed temperature, it may be released when the ash is exposed to a higher temperature.

The average SO_2 emission level of 1600 ppm during the Method 5 test was verified by the Method 6 wet-chemistry technique. (Wet chemistry gave an SO_2 emission level of 1590 ppm.) In addition, as indicated in Table IX, the sulfur balance based on the fuel pellet analysis, the SO_2 emission and the sulfur content in the bottom ash (Table VIII) was complete.

b. CO Levels. CO levels from pellet firing were relatively high compared to those from the firing of conventional stoker coals which are usually <100 ppm. These higher CO levels may be related to the nature of the fuel bed and to the fact that the overfire air flow rate was decreased during the pellet tests. Higher CO levels have been observed in other pellet firings. Because of the compactness of the pellet and the limited access of air into it, the capture process first involves the formation of calcium sulfide via

$$2CaO + FeS_2 \xrightarrow{C} FeO + CO,$$

which can account for part of this increase in CO.

Another possible explanation for the higher CO levels was that the overfire air rate was significantly decreased during pellet firing. In the Battelle boiler the overfire air jets are only 250 mm above the grate. With the increased bed depth from pellet firing, the overfire air jets would have impinged upon the fuel bed if the normal flow rate were maintained. The impingement would increase ash carryover, increasing particulate loadings.

c. Particulate Loading. The Battelle steamplant boiler facility has a mechanical collector to control particulates. Depending on the ash and sulfur content of the coal, the experiments in Phase II showed that particulate loadings varied between 86 and 258 ng/J (0.2 and 0.6 $lb/10^6$ Btu). Generally, for low S, low ash coals, particulate loadings were less than 129 ng/J (0.3 $lb/10^6$ Btu).

The particulate loading from the firing of the fuel pellet was 258 ng/J (0.6 $lb/10^6$ Btu). This loading was not unusually high for a spreader stoker firing a 33-percent-ash coal. This loading should be significantly less for a chain-grate stoker. The smoke opacity was only 20 percent, which would appear low for a particulate loading of 258 ng/J if the fly ash collected was from conventional stoker coal. However, the fly ash from pellet firing is about 50 percent more dense and considerably more coarse than from conventional coals. For equivalent mass loadings, optical density varies inversely with particle size and density. Thus, the apparent discrepancy between smoke opacity and particulate loading is explained partially by laws of optics. As indicated in Table VII, about 19 percent of the fly ash was carbon, a negligible carbon loss.

d. Grate Discharge. Table IX shows that the unburned carbon content in the grate discharge was less than 2 percent. This indicates that the fuel pellets were burned essentially to completion. Analysis indicates that Ca and SO_4 were present and could have combined with water to form a solid mass. Some minor plugging problems were experienced in the ash-disposal system when steam was used to control dusting during transport of the ash.

SUMMARY

The steamplant demonstration indicated the limestone/coal fuel pellet could be fired in an acceptable manner without modifying the facility. During the demonstration, sulfur capture levels that would make the fuel pellet a viable SO_2 control were not achieved. The data suggest that improved SO_2 retention could be realized if bed temperature could be reduced to below 1315 C, perhaps with flue gas recirculation. In addition, a quiescent fuel bed in a stoker boiler may increase the sulfur retention in the bed and should reduce particulate emissions.

SECTION IX

LIMESTONE/COAL FUEL PELLET PROCESS COST SUMMARY

Table X summarizes an economic analysis of the limestone/coal pellet process. This analysis considers costs related to raw materials, utilities, labor, and capital, including profit, interest, and income tax. It indicates a process cost of approximately \$15.40/Mg (\$14/ton) of pellets in addition to the cost of the high sulfur coal. Increased costs of firing the boiler are not considered. As an example of such costs, because of the high ash content of the pellet, ash handling and disposal costs would be higher than for the low-ash conventional coals.

The estimated cost of \$15.40/Mg of pellets above the price of the raw coal is based on the best available data. The cost may vary depending on the type of system used and whether the process may be integrated into a physical coal cleaning preparation plant. This cost is for a product with a heating value of 18.6 KJ/g (8000 Btu/lb) and thus adds about \$0.95 per 10^9 joules (\$1 per million Btu) for SO_2 control. It indicates that the limestone/coal pellet is cost competitive with other control strategies.

BASIC ASSUMPTIONS

The following assumptions were used in the analysis.

- Mine-mouth operation
- Limestone and coal ground to 60 to 100 mesh
- Pellet composition:

  65 percent high sulfur coal
  32 percent limestone
  2 percent pregelenized cornstarch
  1 percent latex emulsion

- Plant capacity of 54.4 Mg/hr (60 tons/hr).

The pellet composition was based on the results of the pellet development effort.

PROCESS FLOWSHEET

The economic analysis was based on the process flowsheet presented in Figure 1. In this process

- Coal is taken from a pile instead of directly from an existing mine operation conveyor
- Limestone is delivered to a pile by truck
- Portland cement is delivered directly to a bin from a truck by pneumatic feeding system suggested by Jeffrey Manufacturing Company
- Relatively long inclined conveyors from the coal and limestone piles are assumed. Costs would be about 35 percent less for horizontal conveyors combined with bucket elevators.
- A paddle-type mixer, as suggested by California Pellet Mill, is used
- California Pellet Mill pelletizers and dryers are costed.

A California Pellet Mill was used in the analysis since cost information was available. However, pellets can be produced by an extruder at perhaps a lower cost. Specifications for processing equipment are given in Table 10.

SOURCES OF INFORMATION

Information on equipment included in the flowsheet was obtained from the following sources:

Front-end loaders — Caterpillar Tractor
Conveyors/elevators -- Jeffrey Manufacturing
Storage bins -- Butler Manufacturing
Feeders -- Jeffrey Manufacturing
Solids mixer -- Rapids Machinery
Pelletizers -- California Pellet Mill
Coolers — California Pellet Mill

COMPARISON TO OTHER CONTROL STRATEGIES

The limestone/coal fuel pellet is an attractive control for two major reasons:

(1) No major modification of the stoker boiler facility is required to fire the pellets

(2) The cost of $15.40/Mg is competitive with other control strategies such as used flue gas scrubbers or low sulfur coals.

The steamplant experiments indicate that neither the stoker boiler facility nor its operation will require major modification to fire fuel pellets. The pellets burn similarly to a lower heating value coal. In contrast, the addition of a flue gas scrubber is a major facility modification and increases system maintenance.

Cost comparisons of the various types of control strategies are difficult to interpret, primarily because of different sets of basic assumptions and different reference points. However, the pellet process costs of $15.40/Mg or $0.95 per 10^9 joules ($1 per million Btu) are competitive with flue gas scrubbers. Foley (7) indicated costs of between $22 and $33/Mg ($20 and $30/ton) of coal for the gas scrubber for small to medium-sized industrial boilers based on 1973 figures.

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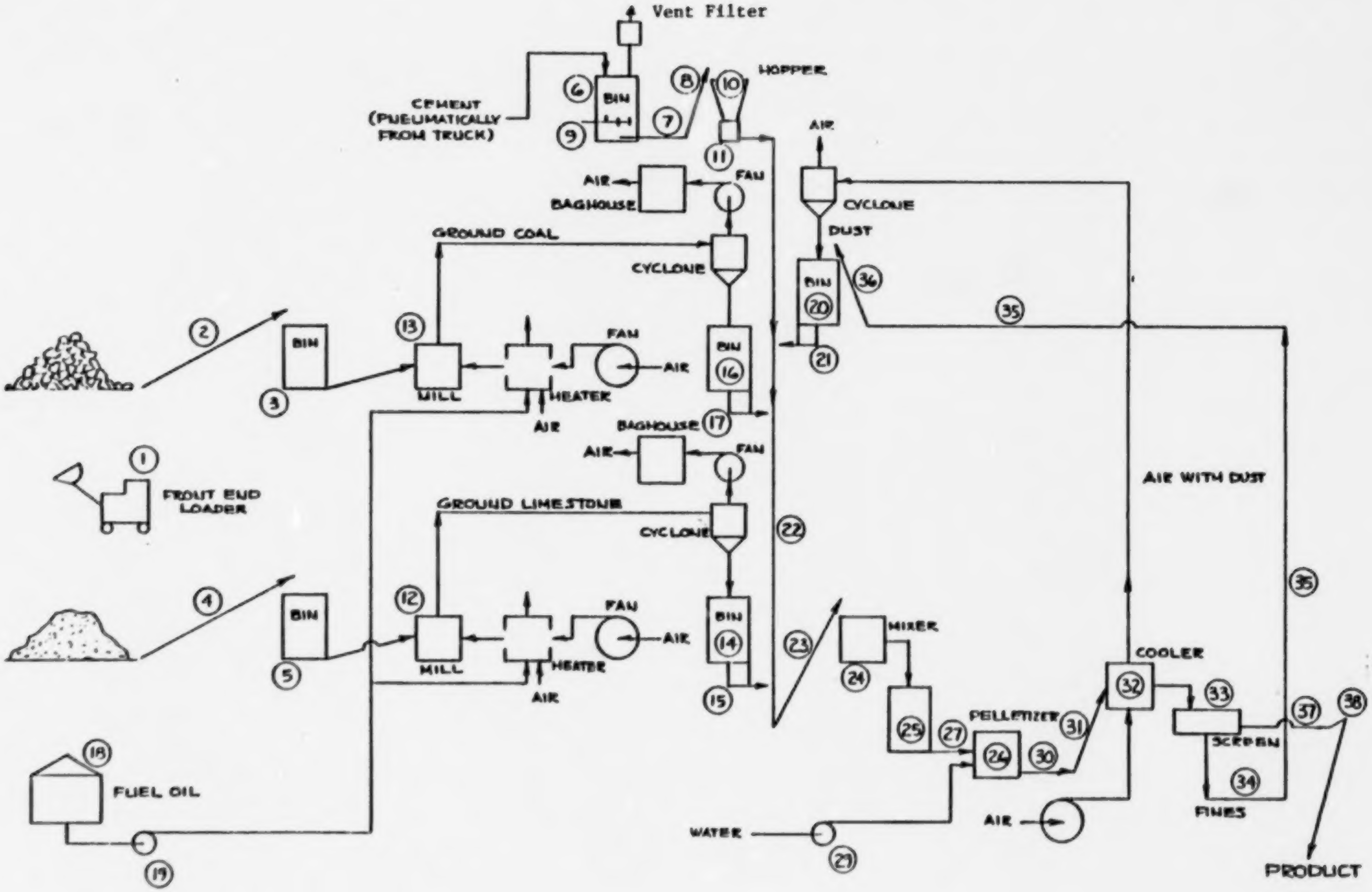
Vent Filter
HOPPER
CEMENT (PNEUMATICALLY FROM TRUCK)
BIN
⑥
⑦
⑧
⑨
⑩
⑪
AIR
BAGHOUSE
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GROUND COAL
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FRONT END LOADER
GROUND LIMESTONE
CYCLONE
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PRODUCT
⑱
FUEL OIL
⑲
WATER
㉙
AIR

FIGURE 1. COAL/LIMESTONE/CEMENT PELLETIZING PROCESS FLOWSHEET

TABLE I. COMPARISON OF PHYSICAL PROPERTIES OF RAW COAL AND FUEL PELLETS

Production Method	Pellet Formulation[a]				Binder	Durability Index[b]	Compression Strength, lb	Weather Index[b]	Post Weathering	
	Coal		Limestone						Durability[b] Index	Strength, lb
	Type	%	Type	%						
Raw coal	Illinois #6	100	--	--	--	85 ± 2	74 ± 12	89 ± 1	75	58
Raw coal	E. Kentucky	100	--	--	--	85 ± 2	83 ± 22	94 ± 1	83	94
Raw coal	Lignite	100	--	--	--	77 ± 4	92 ± 22	80 ± 4	34	45
Raw coal	Rosebud	100	--	--	--	84 ± 2	50 ± 15	79 ± 2	20	68
CPM lab mill	Illinois #6	70	Piqua	30	2% Allbond + 1% Polyco 2136	87	112	100	85	>112
Banner extrusion	Illinois #6	70	Piqua	30	1.5% Allbond 200 + 1% M-167.01	94	84	100	62	60

(a) Water added as needed.

(b) Percent survival = 100 - percent fines.

TABLE II. MODEL-SPREADER STUDIES

Run No.	Fuel	Fuel Size, mm	Ca/S Ratio (Approx)	Average SO_2,[a] ppm	Predicted SO_2, ppm	Average Stack Temp, C	Average Excess Air, percent	Average Sulfur Retention, percent	O_2, percent	CO_2, percent	CO, ppm
7-10-78[b]	50/50 CPM pellets (cement)	12.5 x 19	7	854	3700	340	77	77	9.2	10.9	20
8-10-78[b]	100/50 CPM pellets (cement)	Ditto	4	1116	3700	295	85	70	9.7	11.4	--
79-2	50/50 CPM pellets (cement)	Ditto	7	1040	3700	350	140	72	11.5 - 15.0	5.9 - 8.0	--
79-3	70/30 CPM pellets (cement)	Ditto	3.5	1220	3700	360	110	67	10.0 - 13.8	NA	--
79-4	Medium-S Kentucky	--	0	1050	900	--	120	-15	9.5 - 19	8.2 - 10	150
79-5	Illinois #6 coal	--	0	4120	3700	340	95	-11	8.0 - 12.7	8.4 - 10.8	100
79-6	50/50 CPM pellets (cement)	12.5 x 19	7	1240	3700	300	120	67	13.5	8.5	300
79-7	Illinois #6 coal	--	0	3700	3700	325	100	0	10.6	9.2	100
79-8	70/30 CPM pellets (methocel)	12.5 x 19	3.5	1480	3700	335	90	60	9.5 - 11.5	8.0 - 11.2	150
79-9	70/30 briquets (methocel)	12.5 x 25	3.5	1780	3700	365	80	52	8.2 - 9.8	10.8 - 11.6	85
79-10	70/30 disc pellets (methocel)	12.5 dia	3.5	--	--	--	--	--	--	--	--
79-11	70/30 extrusion (methocel)	--	3.5	1370	3700	375	60	63	7.4 - 9.2	10.8 - 12.6	90
79-12	70/30 CPM pellets (methocel)	12.5 x 19	3.5	1260 (1220)[c]	3700	345	75	67	8.4 - 10.2	10.4 - 12	50

(a) Normalized to 3 percent O_2.

(b) 1978 data.

(c) By Method 6.

TABLE III. ULTIMATE, PROXIMATE, AND ASH-FUSION TEMPERATURE ANALYSES FOR LIMESTONE/COAL FUEL PELLET Ca/S = 3.5

Proximate Analysis (As received), %										Ash-Fusion Temperature, C	
										Initial Deformation	
Volatiles	Fixed Carbon	Moisture	Ash	C	H	N	S	O (difference)	Heating Value, KJ/g	Reducing	Oxidizing
42.9	21.8	2.15	33.2	47.0	3.2	.9	2.9	10.5	18.6	1500+	1500+

TABLE IV. MINERAL ANALYSIS OF ASH

Compound	Percent Weight
Silica, SiO_2	14.20
Alumina, Al_2O_3	5.42
Titania, TiO_2	0.24
Ferric oxide, Fe_2O_3	7.10
Lime, CaO	51.88
Magnesia, MgO	6.94
Potassium oxide, K_2O	0.55
Sodium oxide, Na_2O	0.42
Sulfur trioxide, SO_3	10.77
Phos. pentoxide, P_2O_5	0.09
Strontium oxide, SrO	0.00
Barium oxide, BaO	0.01
Manganese oxide, Mn_3O_4	0.06
Undetermined	2.32
	100.00

TABLE V. COMPARISON OF EMISSIONS FROM COMBUSTION OF A LOW SULFUR COAL AND LIMESTONE/COAL PELLET

Coal Type	Smoke Opacity, percent	CO	NO	Fuel N Converted, percent	SO_2	Fuel S Emitted, percent
Low-S coal	10	70	480	18	540	90
Fuel pellet	20	400	310	20	1800	45

TABLE VI. EMISSION DATA SUMMARY FOR FUEL PELLET DEMONSTRATION

Load, %	O_2, %	CO_2, %	CO, %	NO, %	SO_2, %	Smoke Opacity, %	CO at 3% O_2, ppm	NO at 3% O_2, ppm		Fuel N Converted, %	SO_2 at 3% O_2, ppm		Fuel S Emitted, %	Particulates, ng/J
								Computed	Measured		Computed	Measured		
80	8.4	10.5	300	310	1600	20	420	2250	440	20	4100	2250	55	258

TABLE VII. ANALYSIS OF METHOD 5 FILTER CATCH (Weight Percent)

Ash	C	Ca	CO_3	Fe	Total S
81	19	11	--	4	54

TABLE VIII. ANALYSIS OF GRATE DISCHARGE (Weight Percent)

Ash	C	Ca	CO_3	Fe	Total S
97.7	1.8	36.5	0.7	5.8	3.9

TABLE IX. SULFUR BALANCE

Computed Fuel S In, lb/10^6 Btu	Emitted as SO_2, lb/10^6 Btu	Sulfur Retained in Bed Ash as SO_2, lb/10^6 Btu
7.4 (3182 ng/J)	4.1 (1763 ng/J)	3.3 (1419 ng/J)

TABLE X. SUMMARY OF LIMESTONE/COAL PELLETIZING PROCESS COSTS

Basis: 60 tons per hour product with 65 percent coal, 30 percent limestone, 5 percent Portland cement
23 hours per day, 330 days per year
1380 tons per day, 455,400 per year of product

Fixed plant investment	$2,790,000
Working capital	80,000
Interest during construction	250,000
	$3,120,000

Item	Annual Costs, Dollar	Per Ton Product, Dollars
Raw Materials		
Limestone 18 tons/hr, 136,620 tons/year at $8/ton delivered	$1,092,960	2.4
Pregelatin cornstarch, 9100 tons/year at $20/ton delivered	1,138,500	3.0
Latex emulsion, 1.2 ton/hr, 9100 ton year at $150/ton delivered		
Utilities		
Process water 12 tons/hr (48 gpm) 21.9 MM gallon/year at $0.2/M gal	4,400	0.01
Fuel oil 32 MMBtu/hr, 243 trillion Btu/yr of $3/MMBtu	728,600	1.60
Power 75 percent of 1917 KW or 1440 KW at $0.035/KW-hr	382,500	0.84
Diesel fuel 5 gph, 37,950 gallon/year at $0.80/gal	22,800	0.06
Labor Related		
Direct labor -- 7 operators @ $8/hr plus 25 percent payroll burden ($10/hr total); staffed 365 days/yr	613,200	1.30
Supervision -- 15 percent of direct labor	91,980	.20
Overhead -- 30 percent of direct labor and supervision	306,500	.70
Capital Related		
Maintenance -- 6 percent of fixed plant investment	167,400	0.37
Special pelletizer maintenance at $0.30/ton plus $0.55/ton die and rollers	387,100	0.85
Front-end loader maintenance at $0.22/hr per machine	3,300	0.01
Taxes and insurance -- 1.5 percent of fixed plant investment	41,850	0.09
Depreciation -- 11 year, straight line on fixed plant investment	250,000	0.56
Profit, interest, income tax -- 30 percent of total employed capital	936,000	2.05
TOTAL	$6,167,100	~$14.00

CONTROL OF EMISSIONS FROM RESIDENTIAL WOOD COMBUSTION BY COMBUSTION MODIFICATION

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ABSTRACT

This program was conducted to identify promising methods of reducing emissions of air pollutants from residential wood burning stoves. The overall study has included a review of the few ongoing and recently reported studies related to emissions measurements, causes, and characterization.

The most significant emissions are the hydrocarbons and carbon monoxide released by wood pyrolysis and the carbon monoxide formed by the combustion under locally starved air conditions. The hydrocarbons are especially important as they have been shown to contain polycyclic species which are suspected as being carcinogenic.

An experimental phase of the Battelle program has included stove operations in the laboratory, designed to correlate emissions with design and operating characteristics of the stoves. The burning properties of different types of fuel wood have also been investigated. The combustion tests in radiant stoves have been designed to identify those phenomena which contribute directly and indirectly to the emissions. Continuous monitoring of the following emissions has been provided: O_2, CO_2, CO, NO, SO_2, and total hydrocarbons. In a few tests, batch sampling of stack gases has been performed to determine particulate emissions, and the concentration of polycyclic organic species in both particulate and gaseous emissions. Continuous weighing of the stoves during operation has provided a measurement of burning rate.

The average emission factors for CO and total hydrocarbons varied by more than a factor of 10 between different burning modes and rates. Both emission factors vary inversely with burning rate. At the higher burning rates, the CO constitutes a larger fraction of the emissions

of combustibles. The emission factors also vary inversely with excess air ratio as measured at the stove outlet, although a large fraction of the total air may bypass the active burning zone within most stoves. True down-draft combustion produces low emission factors compared to other modes of burning, especially with a preheated air supply. Nitrogen oxide emissions increase with overall excess air in all the naturally drafted stoves, ranging between 1 and 10 lb/ton fuel.

Combustion modification techniques were found to affect emissions and therefore are of interest for emission controls. These include fuel modifications, thermal and flow modifications in the stove design, and operator techniques.

ACKNOWLEDGMENT

The guidance of the Project Officer, Mr. Robert Hall, is acknowleged and appreciated. The willingness of the Solar Energy Program of the Tennessee Valley Authority to interchange experimental data with this program is also gratefully acknowledged.

INTRODUCTION

As we are all aware, there is a significant increase in the use of wood as a residential heating fuel. This trend was initiated by the rapidly rising prices of oil, public skepticism as to reliability of normal fuel supplies, and the widespread impression that wood burning is environmentally clean. Increased wood use is being encouraged by DOE, equipment manufacturers, and many environmentalists, all with a very limited technology pertaining to emission factors, and even less technical bases for reducing the emission. We have started a program for EPA to identify the effects of several operating variables on objectionable air emissions, and to identify principles of combustion modification that will reduce emission levels from residential wood burning facilities. Unfortunately, the residential stove operator, with his inherent preferences for minimizing his labor and maximizing overall thermal efficiency is adopting stove designs and operating practices conducive to increased emission factors. This accentuates the environmental significance of the continuing increase in quantity of wood burned residentially.

BURNING CHARACTERISTICS OF WOOD

Residential cord wood is generally characterized as either a hardwood or softwood specie, either green or air dried, and normally consists of both split and round pieces. These characteristics all have small but significant effects on emissions. The chemical composition and heating value vary remarkable little between species when measured on a dry basis, the soft woods being only slightly more calorific due to their slightly higher resin content.

The most significant burning characteristic affecting emissions is the phased burning phenomena. The three phases, drying, pyrolysis, and char burning take place successively for any one particle of wood, but all three phases occur simultaneously during most of the burning in a stove. As heat is added to a piece of wood, drying of the surface layer occurs first. This is followed by thermal pyrolysis of this same layer simultaneous with drying of the underlying wood. The pyrolyzed gas may or may not burn at the surface. The effluent steam from the surface drying absorbes both latent and sensible heat. It also tends to block convective heat flow from the surroundings into the wood. This heat flow blockage retards the wood pyrolysis, and thus slows the overall rate of wood burning. As the burning continues and the surface layer becomes converted to a char, pyrolysis gas from the wood below the char layer must diffuse through the charred surface before it can react with atmospheric air to burn in a flame. This subsurface pyrolysis is exothermic, however, and once started can consume a significant portion of the wood without requiring oxidation at the surface or oxygen penetration into the wood. The rate of pyrolytic gas evolution often exceeds the availability of oxygen at the surface resulting in unreacted or partially reacted species leaving the wood even when flames surround each piece of wood. Moisture from the core of the wood can, even in some cases, transpire outward through a hot char layer resulting in CO formation by the water-gas reaction. This primary burning within a pile of wood thus results in incomplete burning, with primary combustion products including CO, and other cellulose and resin pyrolysis products. Subsequent oxidation with a secondary air supply is required to complete the burning. The limited pressure drop normally available in the air supply is usually not sufficient to provide the penetration and mixing required for effective secondary combustion. This results in ultimate emissions of CO, hydrocarbons, and other organics including polycyclic organic materials. Some of these materials condense onto the chimney walls as creosote, some condense into submicron particulates within the stove and chimney passages, and some leave the chimney as a gas. The fraction that is measured as particulates by the Method 5 sampling procedures depends on several factors and is typically only a third or less of the total unburned hydrocarbons leaving the stove. The remainder, which is not deposited in the stack as creosote, presumable condenses onto and into additional atmospheric particulates.

Types of Stoves

There are at least four generic types of naturally drafted wood burning stoves as shown in Figure 1. The designs are catagorized as to the the direction of air flow through the burning wood and wood inventory within the stove. Each of these types is shown in the figure as it can be adapted to provide a secondary air supply and permit secondary burning. Although considered very desireable, effective secondary burning has seldom been attained in the laboratory, and apparently is rarely attained in residential applications. The updraft design appears to be most conducive to organic emissions because the inventory of wood within the stove is extensively heated by primary combustion products depleted of oxygen. The true down-draft burning mode can be very clean burning, when up-flow countercurrents within the bed are prevented. This type of burning delays the rapid release of pyrolysis products until active and complete burning can be achieved.

Other Published Studies

There have been a few programs which have published experimentally measured emissions from wood burning stoves. Professor Butcher at Bowdoin College has measured particulate concentrations after extensive dillution and flue gas cooling in a collection system. He demonstrated that the emission factor for these emissions varied inversely with burning rate and increased linearly with amount of wood charged into the combustion chamber.(1) Monsanto measurements conducted at Auburn University for EPA showed that at fairly high rates of burning the emission factors were nearly independent of specie and moisture content of the wood. The two similar stoves used in that program were not operated in a severely restricted air supply mode, as is prevalent in residential practice. Even so, as much as one third of the carbon fired in the wood was reported emitted as CO.(2) Thus, the increases in organic emissions associated with starved-air or low rate burning were not observed. Extensive measurements of organic species and POM's were made, however, indicating that even at high burning rates these emissions from stoves are appreciably higher than for open burning in a fireplace. Both the Monsanto study and a California Air Resources Board (CARB) study(3) found that at high burning rates the particulates retained on the Method 5 filter were appreciably less than the organic material collected by the back half of the Method 5 system. This indicates that only partial condensation of the organic emissions had occured at the sampling location. The CARB study showed that most emission factors increase with increasing overall excess air. No distinction was noted between excess air within the active combustion zone and air that by-passed the primary combustion zone and simply diluted and quenched the primary combustion products.

EXPERIMENTAL PROGRAM

Facility

The test facility assembled at Battelle for this program consists of three test sites, each with independent, prefabricated, insulated chimneys exhausting within a high bay area in the building. Thus, the chimney effects on draft are not affected either by outside wind or by the building's transient pressure fluctuations. Radiant stoves are mounted on electronic scales, such that total weight losses associated with fuel burning can be continuously monitored. Normal combustion products (CO_2, NO_x and CO) are continuously monitored with NDIR instruments, together with O_2 to determine combustion parameters including excess air and total air flow. Total hydrocarbons (THC) are monitored with a FID instrument calibrated with methane. A high-temperature heated sampling line is used between the sampling probe in the stove outlet and the instrument. This measurement is interpreted as including all organic emissions, whether they ultimately leave as vapor or particulates. Particulate and gaseous samples are collected simultaneously during some tests for POM measurements. This is done at a downstream location in the stack, using a Method 5 front-half filter, followed by a water cooled XAD-2 column. For definitive measurements, filter catches and XAD-2 column catches are separately extracted and analyzed by GC/MS for POM content.

Different fuel woods used have been:

- Commercial oak cordwood, splits and rounds, cured, 20.7 percent moisture
- Commercial pine cordwood, splits and rounds, not cured, 42 percent moisture
- Douglas fir brands 3/4 inch x 3/4 inch on 1 inch centers, oven dried, null moisture
- Oak lumber, nominal 4 inches x 4 inches, cut diagonally, thoroughly air dried, 12.4 percent moisture.

The first two are representative of typical residential fuel, although many stove operators will cure or age their fuel before burning. The fir brands are widely used as a standardized fuel for test purposes. They are very reproducible, easy to ignite, and fast burning. Because of the very high surface area and lack of moisture, the pyrolysis rates early during the brand burning are unusually high. Dried oak, in the 4 x 4 shape, has been used as a fuel closely simulating commercial cordwood in moisture content, size, and shape, yet reproducible to a degree considered satisfactory for test purposes.

Test Procedures

Our usual test procedure is to operate the stove as a batch process, with a test run immediately following a pre-run, burning the same fuel at the same burning rate. The weight loss (fuel burned) and emissions are recorded each minute until the weight loss equals 95 percent of the weight of test fuel fired. Time averages of the measured flue gas compositions are machine calculated for each entire run. Emission factors are then calculated using the averaged gas composition and the weight of wood burned. Effects of a decreasing rate of weight loss (i.e., decreasing burning rate), and the changing composition of the fuel being burned during a run are not accomodated by this calculation technique. Those factors would slightly increase the emission factors, over those calculated by the time averaging technique.

MEASURED EMISSIONS

Emission of Combustibles

Figure 2 shows the time variation of hydrocarbon emissions during a typical run burning the triangular 4 x 4 oak fuel. The total hydrocarbon emissions rose to above 10,000 ppmC (measured as methane) during the early burning, and reduced to less than 1000 ppm when the wood pyrolysis had converted most of the remaining fuel into char. Simultaneously, the O_2 in the flue gas dropped below 5 percent during most of the wood pyrolysis, and increased to about 13 percent during the char burning. This increase in O_2, late in many runs, is assumed to come from an increasing fraction of the primary air flow by-passing the active primary burning area.

In Figure 3 the carbon dioxide and carbon monoxide measurements of the flue gas are shown for the same run. It must be recognized that these flue gas analyses can not be related exclusively to the direct primary combustion effluents, even though no secondary combustion was identified in this run. The secondary air admissions dilute and cool the primary combustion products by an unknown amount, and some of the primary air can bypass the active burning that takes place within the pile of wood.

There appears to be a consistent correlation of CO and hydrocarbon emissions, even though their formation mechanisms are not directly related. Figure 4 shows this relationship as observed in the operation of several stoves operated at different rates of burning. At low burning rates (i.e., stove outlet temperatures below 400 F) the hydrocarbons approximately equal the CO emissions ($HC/CO \approx 1$), whereas at high burning rates (i.e., stove outlet temperatures above about 600 F) the hydrocarbons are only about 1/5 the CO emissions ($HC/CO \approx 0.2$). When these stove emissions get very high, the CO emissions increase relative to the hydrocarbons more than proportionally as these correlations would indicate.

Effects of Burning Rate

Figure 5 shows the effects of burning rate on THC emission factors when burning oak 4 x 4 s in four different stoves. These emission factors were determined from time averaging of emissions measured over a complete burning cycle. It is evident that the emission factors obtained at high burning rates are not representative of stoves operated at the reduced burning rates often used in residential heating.

The combustion in the stoves is air-controlled once the wood is adequately ignited. At reduced rates of air flow into the combustion chamber, caused by partially closing the inlet air damper, a reduced burning rate of fuel is obtained. The reduced wood burning rate is frequently accompanied by increased oxygen content in the flue gas, indicating a larger fraction of the total air flow bypasses the active combustion region. Thus, the restricted air-flow burning is accompanied simultaneously by higher CO and THC emission factors, and higher overall excess air ratios.

Effects of Mode of Combustion

Figure 6 shows a simular plot of the emission factors for a fifth stove, which was altered to permit operation under three different modes of air flow through the primary combustion region. In the updraft mode of burning the primary combustion air entered the combustion chamber through the walls, just above the hearth supporting the burning wood. Combustion products left the top of the chamber, which is the principal characteristic of this burning mode. The local thermal buoyancy effects within the burning wood pile induced the primary flow of combustion air upward through the wood, permitting most of the total air to bypass the active burning area, as is typical in an open fireplace. In the side draft mode the primary combustion products left the primary combustion chamber at the hearth level, thus drawing more of the total air flow through the burning wood. Although CO and THC emission concentrations were appreciably different, the emission factors for these two modes were found to be similar to each other (Figure 6) and similar to the emission factors observed in other stoves (Figure 5).

Also shown in Figure 6 are emission factors observed during several runs with true down draft of air flow through the burning wood. In this downdraft mode, the pile of burning wood was supported on a horizontal grate, with a baffle arrangement forcing all primary air to pass downward through the pile. The burning is intended to occur only adjacent to the grate, the rest of the wood remaining cool. This operation produced low THC emission factors as shown by the test points plotted separately on Figure 6. Visual observations of this downdraft burning were made, sighting through a pyrex window in the top of the combustion chamber. The gas flow velocity and direction were observed by flame velocity and direction within the pile of wood. At lower total air flow rates, the principal down flow of air tended to channel through only one portion of the bed, as local thermally-induced counter flow currents moved upwards through other regions of the bed. This counter flow phenomena tends to defeat a principal advantage of the down flow mechanism: namely isolating the primary combustion products from the inventory of wood thus delaying extensive pyrolysis early in the burning cycle.

It is evident from these observations that the down flow combustion mode has inherent advantages of low emissions, but the down flow is hard to maintain over a wide range of burning rates.

Combustion Air Preheat

While operating a stove in the downdraft mode, a pair of runs was conducted to identify possible effects of preheating of the primary air on emission factors for combustibles. The time averaged emissions for the entire runs were converted to emission factors as shown in Table 1. Oak logs were burned in these runs. Even with the low factors inherent with downdraft burning, reductions were obtained when the primary air was preheated with an outside source. It is not certain if this same effect would be observed with other modes of combustion. In the downdraft mode of burning the heated incoming primary air should have the greatest effect, by promoting early pyrolysis of wood thus adversely affecting emissions of combustibles. However, these pyrolysis products can not easily bypass the active burning area at the downstream edge of the bed as in other modes of combustion. Reductions in emission factors were observed as shown in Table 1.

Preheating secondary air is assumed to have no effect on emissions unless secondary combustion is established or can be initiated by the preheat. When burning wood which emits large quantities of combustibles early in a burning cycle (dry fir brands) secondary combustion was initiated when a 5 scfm stream of 442 F secondary air was admitted. This constituted about 15 percent of the total air supply, and resulted in a small reduction in the previously very high THC emissions.

Nitrogen Oxides Emissions

Although NO_x emissions have not generally been recognized as a serious emission from wood stoves, they should be considered. The temperature levels within the stoves are not expected to reach the range where fixation occurs. Although the nitrogen content in wood is not high, the conversion of this nitrogen can be significant. Accordingly, our laboratory instrumentation included a monitor for NO_x (as NO) during the test runs.

Figure 7 shows the experimental correlation of average NO_x emission factors with the time averaged oxygen content of the flue gas leaving the stove. It must be recognized that the excess air or oxygen content leaving the combustion chamber is only an upper limit as to what prevails within the burning pile of wood, as in most cases there is no measure of how much of the primary supply bypasses the primary burning region, or how much secondary air is supplied which only dilutes the primary combustion products.

Commercial Low Emission Burner

A residential wood burning appliance has been developed under a DOE contract by Professor Hill at University of Maine. The burner demonstrates that increased efficiencies can be obtained with an improved design of the combustion and heat recovery system. The burner is a residential boiler (water heater) for a central heating system that incorporates several factors beneficial in controlling air pollution emissions. The combustion is supported by both forced draft of combustion air and induced draft of flue gases, such that a high turbulence level can be maintained in the burning areas, yet not develop a firebox pressure exceeding ambient. It operates only at a fixed, relatively high burning rate (∿150,000 Btu/hr) comparable to one of the large radiant heaters. Several characteristics of this design favor low THC and CO emissions:

- High turbulence level in primary burning area
- Primary combustion products isolated from inventory of wood
- Inventory of wood cooled by water-walled chamber
- Burning confined to small portion of the wood inventory
- Refractory lined primary combustion area
- Refractory lined secondary combustion area
- Large pieces of wood utilized to reduce excessive pyrolysis early during burning cycle
- Burning restricted to high rates, with heat storage provisions to accomodate lower heating requirements.

A commercial production version of this design of wood burner was obtained and operated in the laboratory. Table 2 presents the operating conditions and the significant emissions. During the batch burning, the overall excess air remained high, with an average oxygen content exceeding 10 percent. The heat recovery efficiency remained high (low stack temperatures) because a large and effective heat transfer surface is provided for the flue gas to water heat exchange within the boiler.

Table 2 summarizes the emissions performance of this boiler, together with corresponding data from a radiant heater operating in the up draft mode presented for comparison.

TECHNIQUES FOR REDUCING EMISSIONS

In reviewing the observations of stove performance on this and other experimental programs, several combustion modification techniques have been identified which show promise of reducing objectionable emissions. In summary, they are listed below with a few less promising noncombustion techniques. Most of these techniques still need further development before they can be reliably reduced to practice, especially in the simultaneous application of several techniques. Both the prevention of the initial pollutant formation and destruction of the formed pollutants before their emission from the stove are considered. Some of these approaches are in conflict with operator convenience or overal thermal efficiency of the stove, however, any reduction in hydrocarbon emissions from the stove will reduce creosote problems in the chimney. The forced draft boiler described previously is an example of the simultaneous application of several of these techniques.

Modifications of Fuel

- Utilize a processed wood (pellets or briquettes) to permit continuous fuel flow into and/or within the stove. Active burning can then be contained within a small volume permitting better controls, even to the extent of developing truly fuel-controlled burning.

- Reduce volatility of the wood, especially at low temperatures, either by thermal processing (charring) before burning, or possibly with additives or fuel admixtures.
- Reduce moisture content, if other provisions are made to limit excessive pyrolysis when initially heated.
- Incorporate additives to lower ignition temperature of hydrocarbons leaving primary combustion space.

Modifications of Stove Design, Thermal Control

- Insulate or cool the inventory of wood in the stove prior to active burning to minimize premature pyrolysis
- Insulate active combustion zone(s) to aid in ignition and burning of pyrolysis products by increasing the temperature level
- Preheat the air supplied to active burning zone(s) without pyrolyzing the wood inventory within the stove.
- Provide recoverable heat storage for stove output, to permit a high rate of burning to satisfy low rate heat demands. This can be either integrated within a stove or as an add-on component, utilizing sensible and/or latent heat storage.
- Add supplemental fuel, supplemental air, or both to the secondary combustion system to just assure complete burning of combustible emissions from the primary burning zone. The supply requirements for these supplements change appreciably during a burn cycle, requiring a sophisticated sensing and control system.

- Provide an afterburner system, independently fueled with balanced fuel and air supplies, which will consume all combustible emissions as their emission rate changes during a burn cycle.
- Provide a heat path from primary burning zone to the secondary burning zone, to assure ignition when combustible mixtures are obtained after introduction of secondary air.

Modification of Stove Design, Air Flow Control

- Supply energy to the air supplies to provide control, turbulence, and mixing in the primary and secondary combustion zones, as by the use of a forced and/or induced draft fan.
- Control flow of primary air within the stove to minimize the extensive by-passing of the active burning zone, especially at low burning rates.
- Mix secondary air with the primary combustion products immediately as they leave the burning wood.
- Prevent combustion products from convectively heating the entire inventory of wood within the stove.
- Change combustion chamber geometry when operating at reduced burning rates to maintain a high rate of burning per unit volume. Movable baffles or dummy removable side walls would be one approach.
- Terminate secondary air supply thus increasing primary air supply when flue gas dilution is the only effect realized. This may also require a complex sensing system.

Modification of Operator Techniques

- Avoid excessive quantities of wood within the stove at one time.
- Use large pieces of wood after burning is established, consistent with desired rate of burning.
- Operate only at high burning rates, with shutdown times between burns to accommodate lower heating requirements (i.e., intermittent stove operation).

Add-On Devices

- Heat storage device as noted above
- Direct combustion afterburner as noted above
- Catalytic afterburner
- Electrostatic precipitator
- Scrubber.

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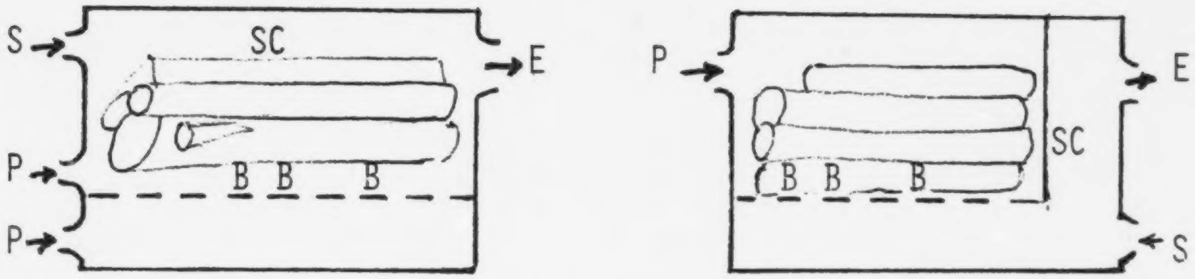
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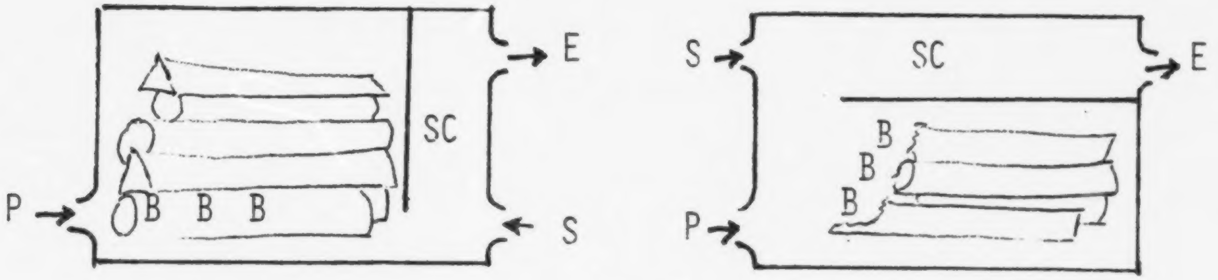
OR UP DRAFT

DOWN DRAFT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CROSS DRAFT

S-FLOW

TYPES OF STOVES
ACCORDING TO
AIR FLOW PATHS

P - PRIMARY AIR SUPPLY
S - SECONDARY AIR SUPPLY
E - EXHAUST TO STACK
B - PRIMARY BURNING
SC - SECONDARY COMBUSTION

FIGURE 1. GENERIC DESIGNS OF WOOD STOVES BASED ON FLOW PATHS

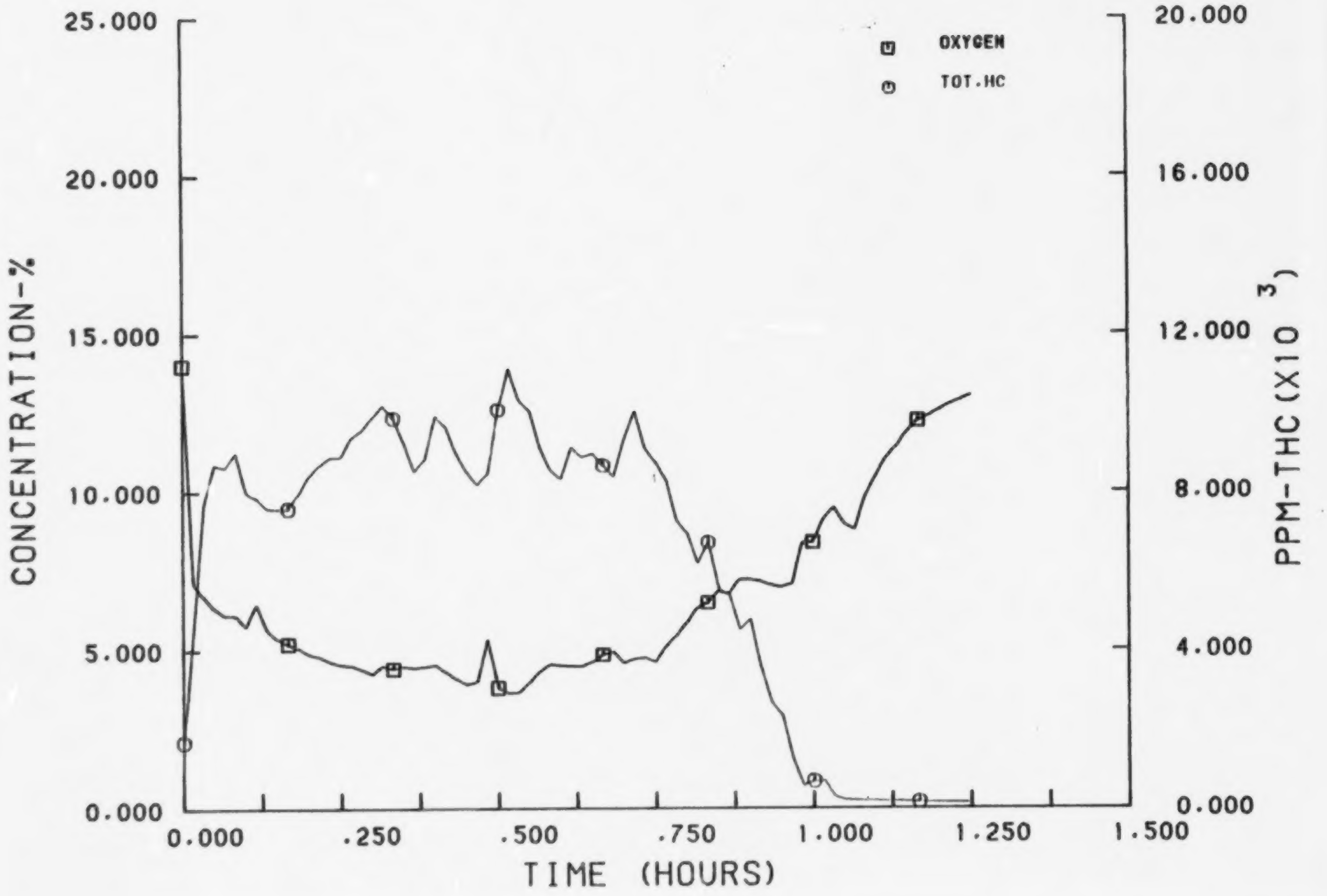

FIGURE 2. HYDROCARBON EMISSIONS DURING A RUN BURNING CURED OAK

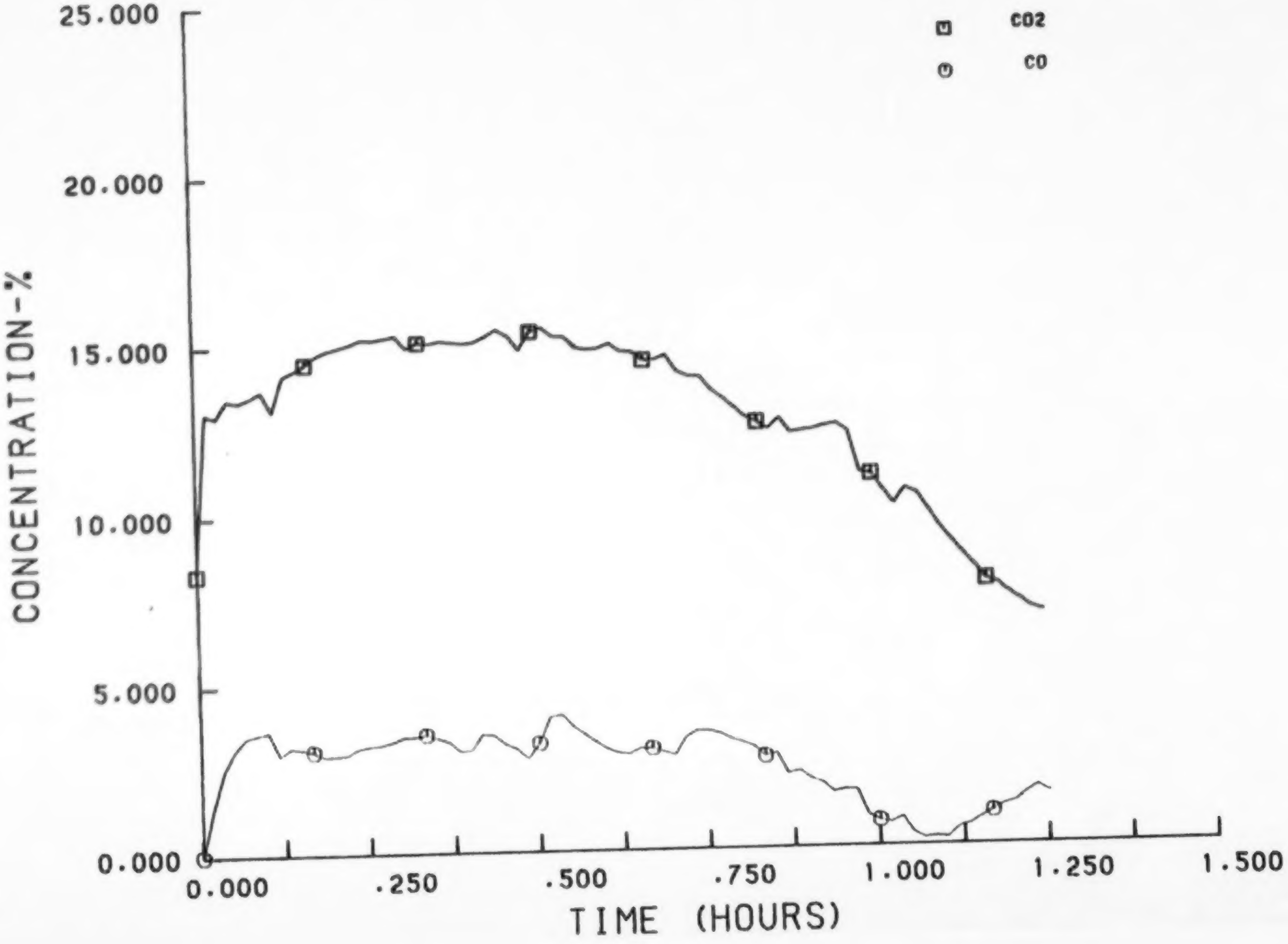

FIGURE 3. CARBON MONOXIDE EMISSIONS DURING A RUN BURNING CURED OAK

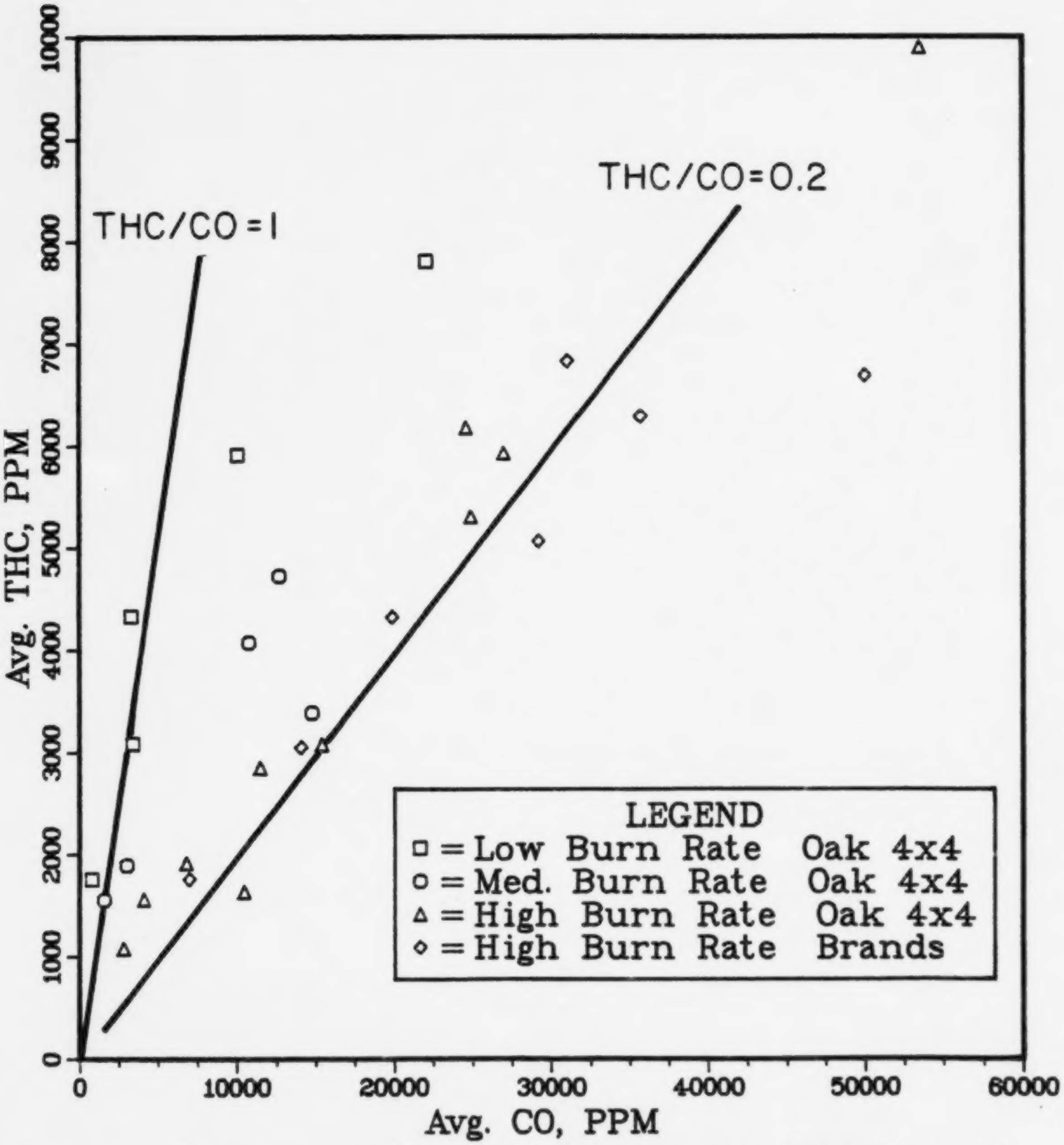

Fig. 4 Correlation of THC and CO Emissions for Several Stoves

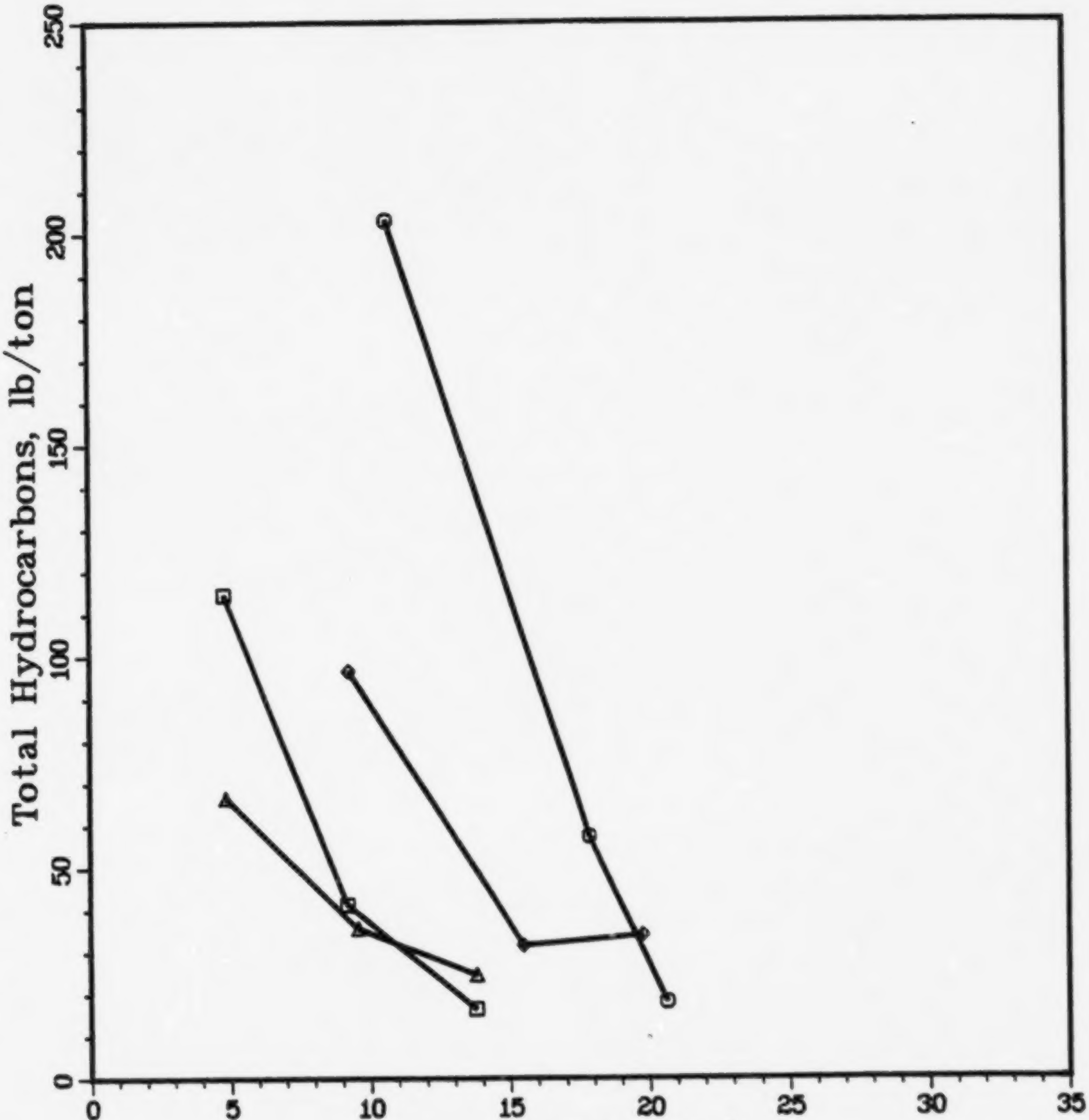

Fig. 5 THC Emission Factors for Several Stoves

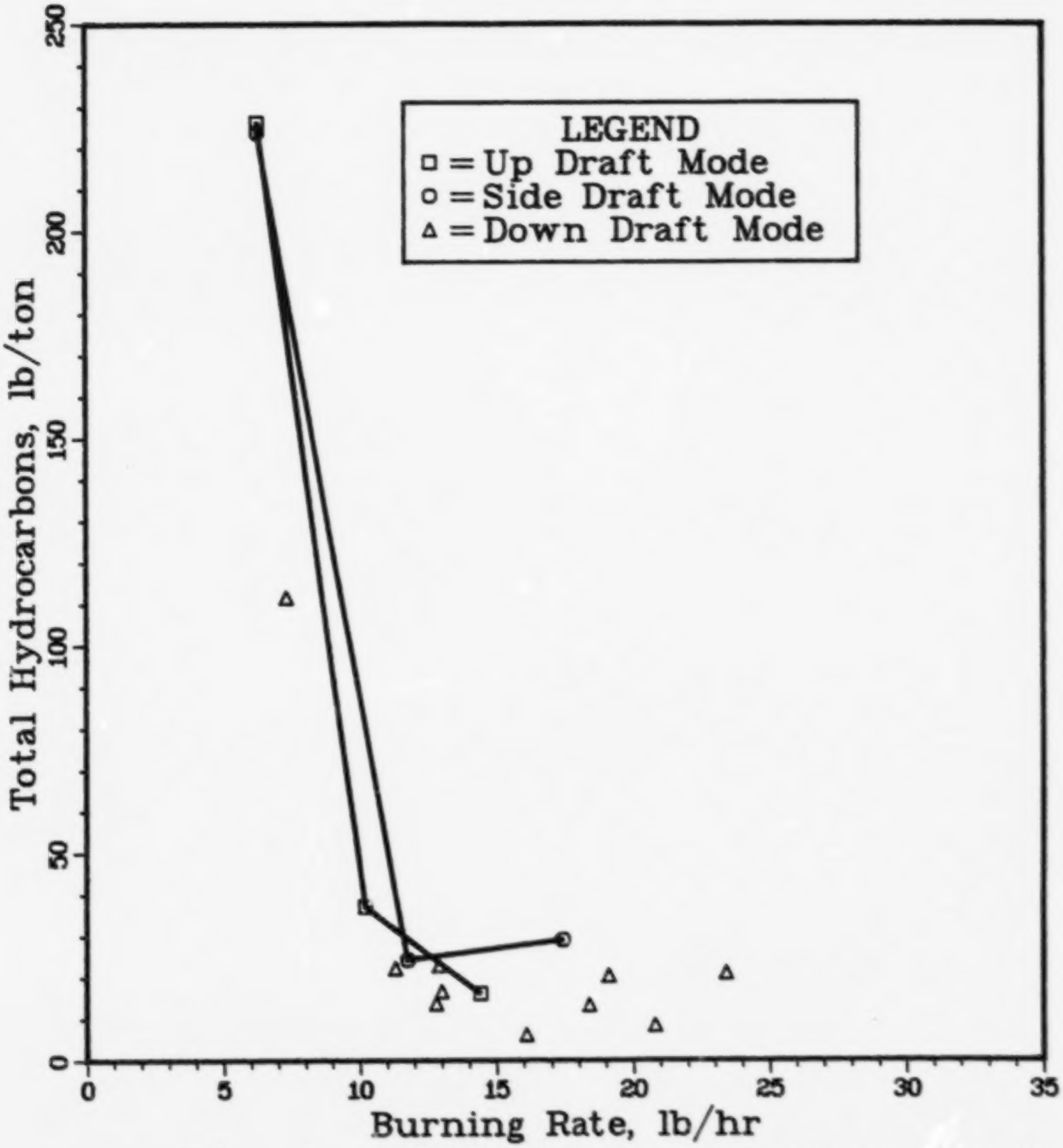

Fig. 6 THC Emission Factors for One Stove, Three Modes of Burning

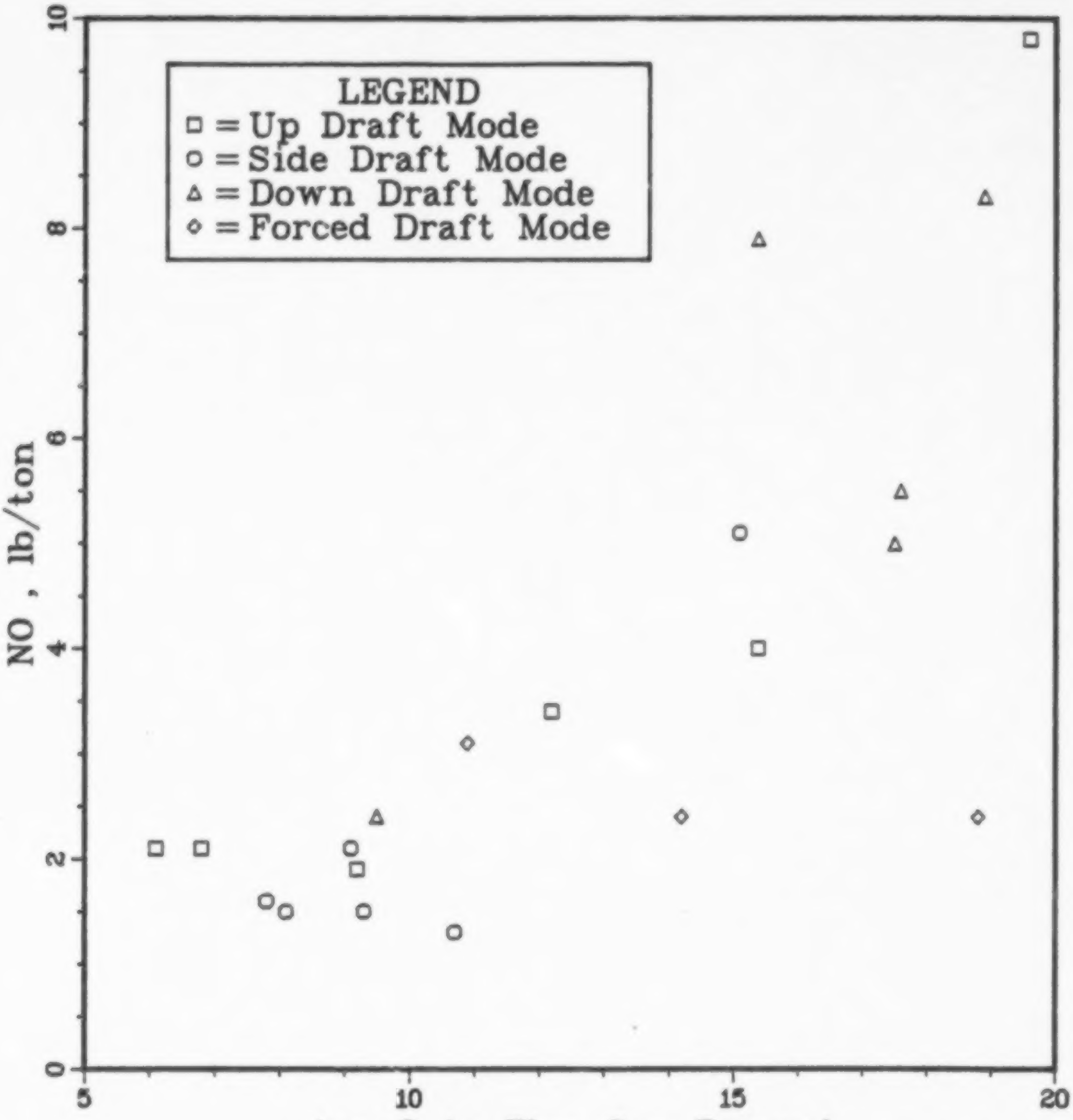

Fig. 7 NO Emission Factors for Different Modes of Burning

FIELD TESTS OF ELEVEN STOKER COAL-FIRED BOILERS FOR EMISSIONS CONTROL AND IMPROVED EFFICIENCY

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ABSTRACT

This stoker test program was awarded to the American Boiler Manufacturers Association (ABMA) in late 1977 as a result of the national interest in coal utilization. The objective of the program is to improve specification data relating to emissions and efficiency of coal fired stoker boilers. Such data are required by both industry and government in order to increase coal usage.

Eleven stoker boilers were tested including six spreader stokers, one vibragrate stoker and four overfeed traveling and chain grate units. Each units emissions and efficiency were measured under a variety of operating conditions. This paper deals with particulate loading, nitric oxide concentration and combustibles in the bottom ash and flyash. The effect of stoker design, boiler loading, excess air, overfire air and coal properties on the three types of emissions cited above is also discussed.

Test results show that overfeed stokers have lower particulate and nitric oxide emissions, and lower combustible heat losses than do spreader stokers. Flyash reinjection is shown to substantially increase particulate loading in some cases. Overfire air is shown to have little or no effect on nitric oxide emissions, and flyash combustible content is a function of particle size. These and other relationships are discussed. More importantly, an attempt is made to quantify these relationships and provide a broad data base from which government and industry may draw to implement sound decisions for our coal future.

Field testing was completed in late 1979. Individual site reports are available through the EPA or NTIS. A final project report is scheduled for completion in late 1980.

SECTION 1

INTRODUCTION

This paper outlines the objectives and presents some of the preliminary findings of a coal-fired stoker test program. The program was initiated because in recent years there has been a preponderance of industrial boiler installations which have been shop-assembled gas- and oil-fired units purchased and installed at substantially lower costs than conventional coal burning, boiler-stoker equipment. Because of this decline in coal-firing, little or no work was done to improve specification data and information for consulting engineers and purchasers of coal-burning equipment. The current implementation of more rigid air pollution regulations has made it difficult for many coal-burning installations to comply with required stack emission limits, thus creating a further negative influence on coal-firing.

The market for coal suitable to be fired in industrial boilers, as reflected by sales data, is being held back by critical uncertainties in the environmental and energy areas, causing potential customers of coal-fired industrial boilers to shelve plans for capital expansion and conversion. This has caused a serious reduction in the number of installations of new industrial coal-fired units. It is highly desirable to remove these uncertainties and thereby establish confidence among industrial users to order and install stoker coal-fired boilers. This will lead to significantly increased coal usage.

OBJECTIVES

The objectives of this Program are:

1. To prepare a comprehensive project report: Design and Application Guidelines for Industrial Stoker Firing.

2. To advance boiler and stoker technology by testing various boiler furnaces and stoker designs for response to changes in coal analysis and sizing, degree of flyash reinjection, overfire air admission, ash handling and pollutants emitted.
3. To refine applications of existing pollution control equipment and to more closely control stack emissions under varied operating conditions through more accurate boiler outlet dust loading data.
4. To contribute to the design of new and improved air pollution control equipment.
5. To facilitate preparation of reasonable and workable national emissions standards for small coal-fired boilers by the Environmental Protection Agency.
6. To facilitate planning for coal supply contracts by users of the boiler/stoker equipment by developing reasonable emission regulations.
7. To promote the increased utilization of stoker coal-fired boilers by U.S. industry by insuring the compatibility of these units emissions with appropriate environmental requirements.

AWARD OF CONTRACT

This stoker test program was awarded to the American Boiler Manufacturers Association (ABMA) in late 1977 as a result of the national interest in coal utilization. The program is sponsored by the Department of Energy (DOE) under Contract Number EF-77-C-01-2609, and co-sponsored by the Research Branch of the United States Environmental Protection Agency (EPA), under inter-agency Agreement Number IAG-D7-E681. The program is directed by an ABMA Stoker Technical Committee which, in turn, has subcontracted the field testing to KVB, Inc., of Minneapolis, Minnesota.

SITE TESTING

The test program involved testing eleven coal-fired stoker boilers. The boilers ranged in size from 13 to 87 megawatts thermal output (45-300 K lb steam/hr). Six were spreaders, one was a vibragrate, and four were overfeed traveling grate and chain grate units. Most of the boilers were new "state-of-the-art" designs.

Extensive testing has been completed on all eleven boilers listed in the table below. The ownership and location of these boilers is being treated confidentially.

LISTING OF UNITS TESTED

Site Code	Boiler*	Stoker	No. Coals	Arrangement of Heat Trap
A	87 MW FW	Detroit Spreader	3	Econ. after ESP
B	61 MW Riley	Riley Spreader	4	Econ. after DC
C	59 MW B&W	Detroit Spreader	3	Econ. after DC
D	25 MW B&W	Detroit Vibragrate	3	Econ. before DC
E	55 MW Riley	Riley Spreader	3	Econ. before DC
F	24 MW Keeler	Detroit Spreader	2	Econ. before DC
G	22 MW Zurn	Zurn Spreader	3	No economizer
H	13 MW Bros	Riley Traveling Grate	1	No economizer
I	21 MW Wickes	Riley Traveling Grate	2	No economizer
J	21 MW Keeler	Laclede Chain Grate	2	Econ. before DC
K	15 MW Riley	Riley Traveling Grate	2	Econ. before DC

*MW is megawatts thermal output;
$MW_T x3.4 = 10^6 Btu/hr = 10^3 lb/hr$ Steam

The boilers were tested for particulate and gaseous emissions and for boiler efficiency over a wide range of firing conditions. Particulate mass loading was determined at the boiler outlet and after the mechanical dust collector (if any). Other tests included, but were not limited to, O_2, CO_2, CO, NO, SO_2, SO_3 and particle size distribution. Percent coal fines was determined for most tests, and coal and ash samples were collected for chemical analysis.

SECTION 2

TEST RESULTS

Comprehensive results of this test program are being published by the Environmental Protection Agency (EPA) and are available through the EPA at Research Triangle Park, or through NTIS (1-8). This paper deals with nitric oxide and particulate emissions, and with the combustible content of bottom ash and flyash.

PARTICULATE LOADING

A total of 291 particulate mass loading determinations were made in field tests on the eleven stoker boilers. Most of these tests were simultaneous measurements made before and after the mechanical dust collector. From this large data base it is possible to make several generalizations about the variables affecting particulate loading.

Stoker Design

Stoker design is a variable which had a major impact on particulate loading. For example, spreader stokers emitted five times more particulate matter at the boiler outlet than did overfeed stokers. Also, spreader stokers with flyash reinjection emitted as much as four times more particulate matter than spreader stokers without reinjection, when measured at the boiler outlet. These results were true regardless of the size of the unit.

The range of particulate loadings measured at the boiler outlet under full load conditions were as follows:

	Boiler Outlet Particulate Loading
Spreader's with Reinjection	4300-15500 ng/J (10-36 lb/10^6Btu)
Spreader's w/o Reinjection	1200- 3100 ng/J (3-7 lb/10^6Btu)
Overfeed's w/o Reinjection	260- 950 ng/J (0.6-2 lb/10^6Btu)

These differences were not as distinct downstream of the mechanical dust collector. Collector efficiency, which is sensitive to particle size distribution and inlet loading, was highest for spreader stokers with flyash reinjection and lowest for overfeed stokers. The range of particulate loadings measured downstream of the mechanical dust collector under full load conditions were as follows:

	D.C. Outlet Particulate Loading
Spreaders with Reinjection	200-470 ng/J (.47-1.1 lb/10^6Btu)
Spreaders w/o Reinjection	70-600 ng/J (.17-1.4 lb/10^6Btu)
Overfeeds w/o Reinjection	50-320 ng/J (.11-.75 lb/10^6Btu)

Boiler Loading and Excess Air

The particulate loading at the boiler outlet always increased as load increased, sometimes doubling between loads of 50% and 100% of capacity.

The boiler outlet particulate loading also increased when excess air was increased. The data base for this observation are few and the magnitude of the increased particulate loading has not yet been quantified.

Overfire Air

The data indicate that high overfire air flow rates, representing 10% to 20% of the total combustion air, are best for minimizing particulate loading. When overfire air flows were increased from their lowest non-smoking flow rates to their maximum flow rates, particulate loadings were observed to either decrease or remain unchanged.

DROP IN PARTICULATE LOADING DUE TO INCREASED OVERFIRE AIR

Spreader Stokers		Overfeed Stokers	
Site A:	25-50%	Site D:	No Change
Site B:	25%	Site H:	50%
Site C:	No Change	Site I:	40%
Site E:	No Change	Site J:	No Change
Site F:	35%	Site K:	No Change
Site G:	No Change		

Coal Properties

Although several coals were test fired at each site, with only one exception, their varying chemical properties had little or no effect on particulate loading. Even at Test Site C where an Eastern coal and a Western coal were fired in the same boiler, no change in particulate loadings was observed. It is recognized that in most cases the coals chemical properties were very similar and that these results apply only to the specific coals tested.

Physical coal properties did make a difference. An increase in the percentage of fines in the coal, at Site K, resulting from passing a washed 0x1-1/4" coal through a crusher set at 3/4", increased the particulate loading by 60% at full load. The same coal unwashed and reported to have a high clay content gave a 180% higher particulate loading than when washed. These data are graphically presented in Figure 1.

NITRIC OXIDE

Nitric oxide levels were measured for 389 test conditions during the test program. From this large data base, several correlations can be made between nitric oxide concentration and the test variables.

Stoker Design

Spreader stokers emitted significantly higher levels of nitric oxide than did overfeed stokers at the same load and excess oxygen. This point is clearly illustrated in Figure 2 where nitric oxide levels are 1-1/2 to 2 times higher for spreaders. Even when correction is made for the fact that overfeed stokers are operated at higher excess oxygen levels than spreader stokers, the spreaders emit 50% more nitric oxide per MMBtu.

	Average Full Load O_2	Average NOx
Spreader Stokers	6.4%	206 ng/J (0.48 lb/10^6Btu)
Overfeed Stokers	7.9%	133 ng/J (0.31 lb/10^6Btu)

Boiler Loading and Excess Oxygen

At constant load, a one-percent increase in excess oxygen resulted in an average .048 lb $NO_2/10^6$Btu increase in NOx. This slope was true for both spreader stokers and overfeed stokers as illustrated in Figure 2.

At constant excess oxygen, nitric oxide increased with increasing load. This relationship has not yet been quantified, but it is observed that the effect is greater on spreader stokers than on overfeed stokers.

Since excess oxygen decreases as load increases under normal stoker operation, these two influences tend to cancel each other out. Therefore, under normal operating conditions, nitric oxide concentrations are invarient with load.

Overfire Air

In general, changes in overfire air operation had no effect on nitric oxide concentrations. Specific units tested showed small increases or decreases in nitric oxide as the overfire air flow was altered, but no consistent trend was established.

Flyash Reinjection

Flyash reinjection did not alter the nitric oxide concentrations. This was observed on all three of the spreader stokers which reinjected flyash from their mechanical dust collectors.

Coal Properties

Nitric oxide concentration was invarient with coal properties in these tests. The one exception to this rule, a 36% reduction in nitric oxide when switching coals at Site I, is suspect.

Although many of the coals tested were very similar, a few do stand out as true tests. For example, at Site C a Western coal and an Eastern coal with significantly different chemical composition were test fired in the same boiler. At Site K, coal fines and clay content were major variables. In both these case studies, nitric oxide concentration remained the same.

COMBUSTIBLES IN THE ASH

Combustibles in the ash are important since they are related to boiler efficiency. They are of special concern in stoker boilers where they result in heat losses often exceeding 5% of the unit's heat input.

A total of 511 ash samples were collected and examined for their combustible content in the course of this test program. These samples included bottom ash, flyash from before and after the mechanical dust collector, and flyash from the mechanical dust collector hopper.

Stoker Design

The magnitude of the combustibles in the ash was found to correlate with stoker type. For example, spreader stokers had less combustible material in their bottom ash than did overfeed stokers. However, spreader stokers had more combustible material in their flyash than did overfeed stokers. Figures 3 and 4 illustrate this correlation.

The net result was that spreader stokers without flyash reinjection had combustible heat losses which were several percent greater than those for overfeed stokers. With flyash reinjection, some of this loss is recovered, but not all.

	General Combustible Heat Loss Range
Spreader with Reinjection	2-6%
Spreader w/o Reinjection	4-7%
Overfeed w/o Reinjection	2-4%

You will notice in Figure 4 that combustibles in the flyash of Site C were considerably lower than they were in the flyash from the other spreader stokers. The reason for this low combustible level has not been established, but it is believed to be related to boiler design parameters.

The boiler at Site C was designed with a very low heat release rate of less than 500,000 Btu/hr-ft^2 effective grate area. This is considerably lower than the 600,000 to 850,000 Btu/hr-ft^2 of the other spreader stokers tested. The Site C heat release per front foot of grate width was also lowest in the group. These two design parameters may be at least partially responsible for the low combustible levels at Site C.

Boiler Loading and Excess Air

Combustible levels were relatively invarient with load. In general they showed a slight tendency to increase as load increased, but the opposite trend was also observed in a few isolated cases.

The effect of excess air on combustibles has not been fully examined, but preliminary indications are that this variable had little effect on combustible levels as long as excess air was maintained within a normal, non-smoking range.

Overfire Air

Increasing the overfire air pressure has a tendency to reduce the combustible content of the flyash. This reduction is presumably due to improved fuel-air mixing in the flame zone.

Our examination of the relationship between overfire air and combustibles in the bottom ash is not complete. However, it appears that combustibles in the bottom ash increased at a few sites when overfire air flow was increased.

Flyash Reinjection

Combustible levels in the bottom ash and the flyash were unchanged by flyash reinjection status.

Coal Properties

Combustibles in the ash showed a correlation with coal properties at only one site in this program. At Test Site C, where an Eastern and a Western coal were fired in the same boiler, the Western coal had the highest percentage of combustibles in its bottom ash and the lowest percentage of combustibles in its flyash.

Combustibles vs Size

The combustible content of flyash is a function of the size of the flyash particles. The largest particles contain the highest percentage of combustible matter.

Although not a part of the original scope of this program, a limited investigation was undertaken to quantify this relationship. Selected samples of flyash were sieved into several size fractions and analyzed for their combustible content.

The results are plotted in Figure 5. The two plots shown relate combustible content to partice size for two unrelated boilers and two different ash sample locations. Each plot presents the average of data from four samples. They have one thing in common, the larger particles contain the highest combustible content.

Since mechanical dust collectors remove the largest particles and allow the smallest particles to pass on through, one would expect the exiting particles to contain a lower combustible content. Test data from the six spreader stokers verifies this assumption and illustrates the magnitude of the combustible drop.

	Percent Combustibles in Flyash	
	D.C. Inlet	D.C. Outlet
Site A	58%	30%
Site B	60	29
Site C	25	16
Site E	66	52
Site F	67	47
Site G	53	32

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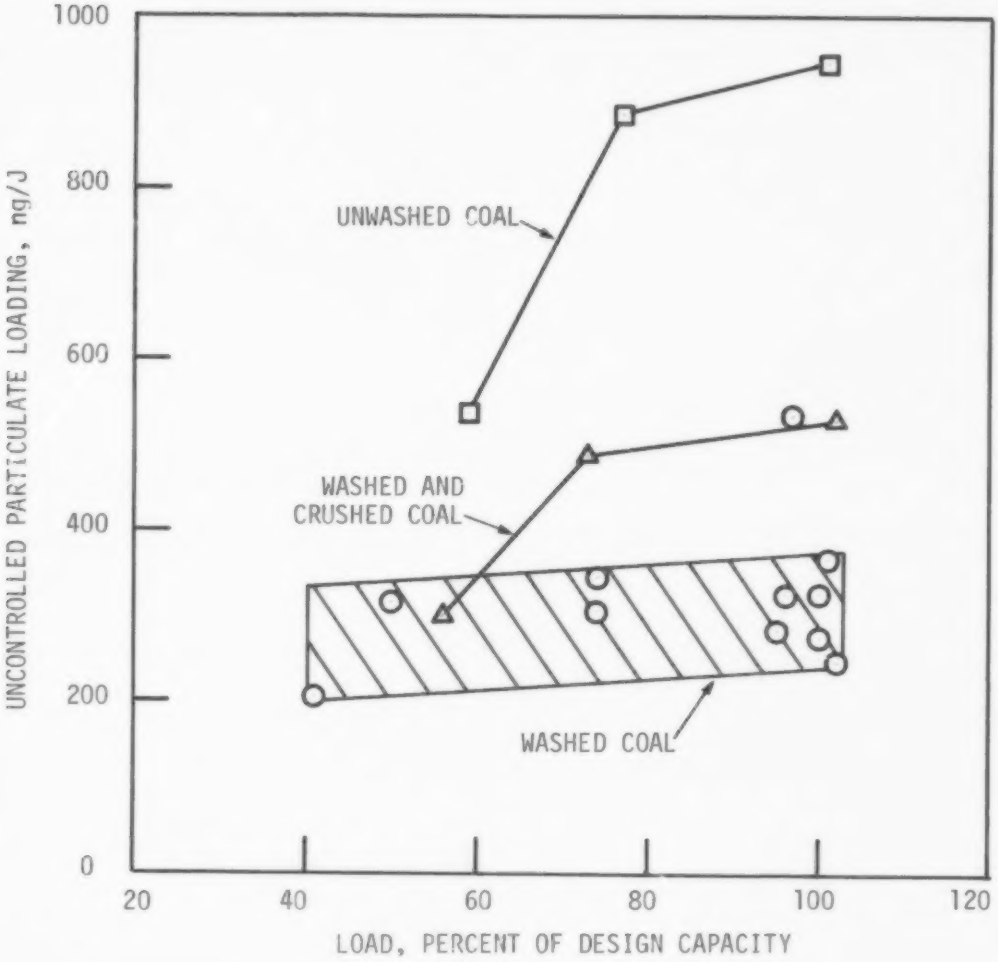

Figure 1. Relationship Between Uncontrolled Particulate Loading and Boiler Load for Three Forms of Coal from the Same Mine Fired at Site K.

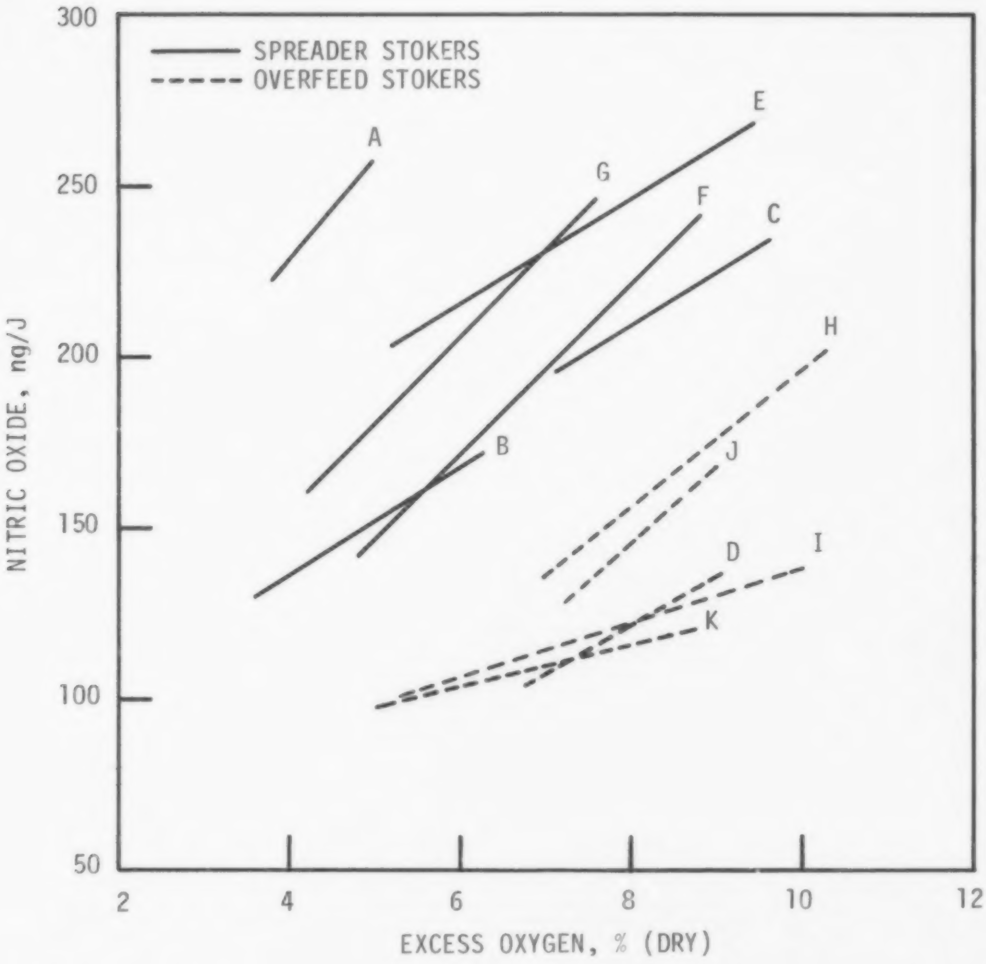

Figure 2. Relationship Between Nitric Oxide Concentration and Excess Oxygen at Maximum Load for Eleven Stoker Boilers.

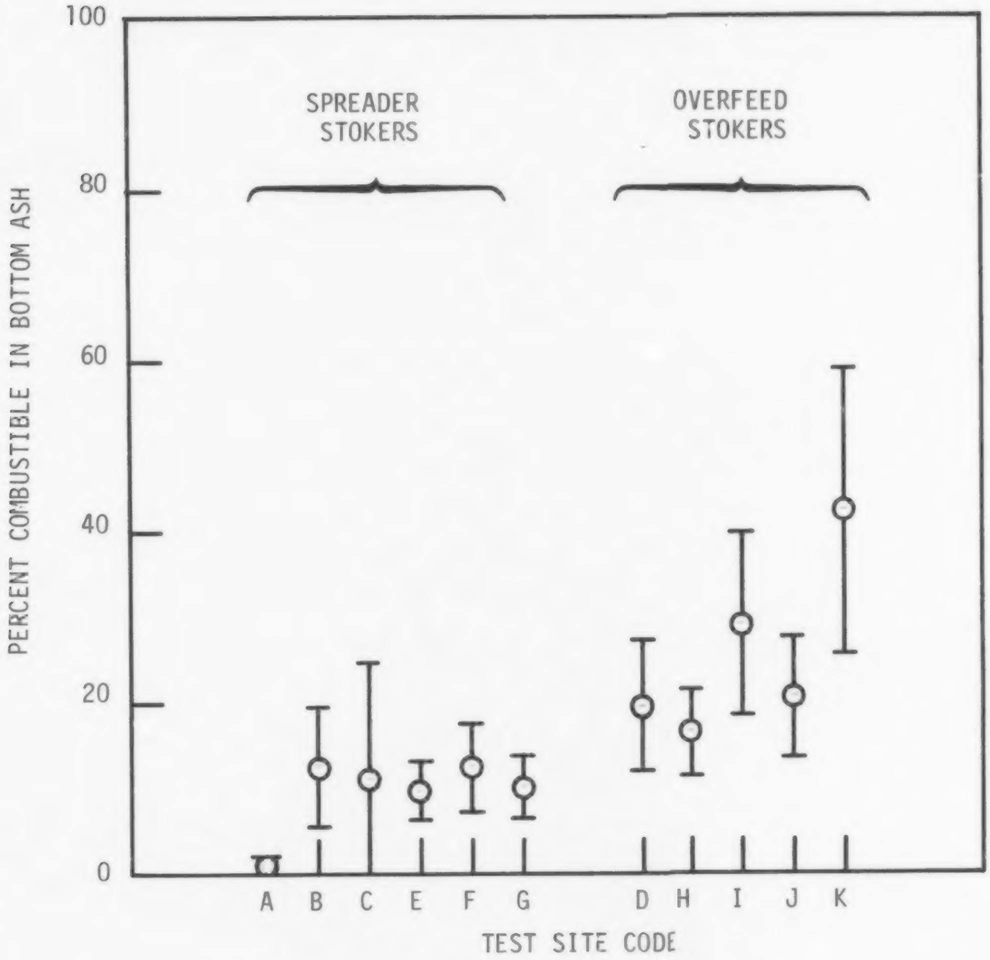

Figure 3. The Average and Standard Deviation of the Mass Percentage of Combustible Material in the Bottom Ash of Eleven Stoker Boilers.

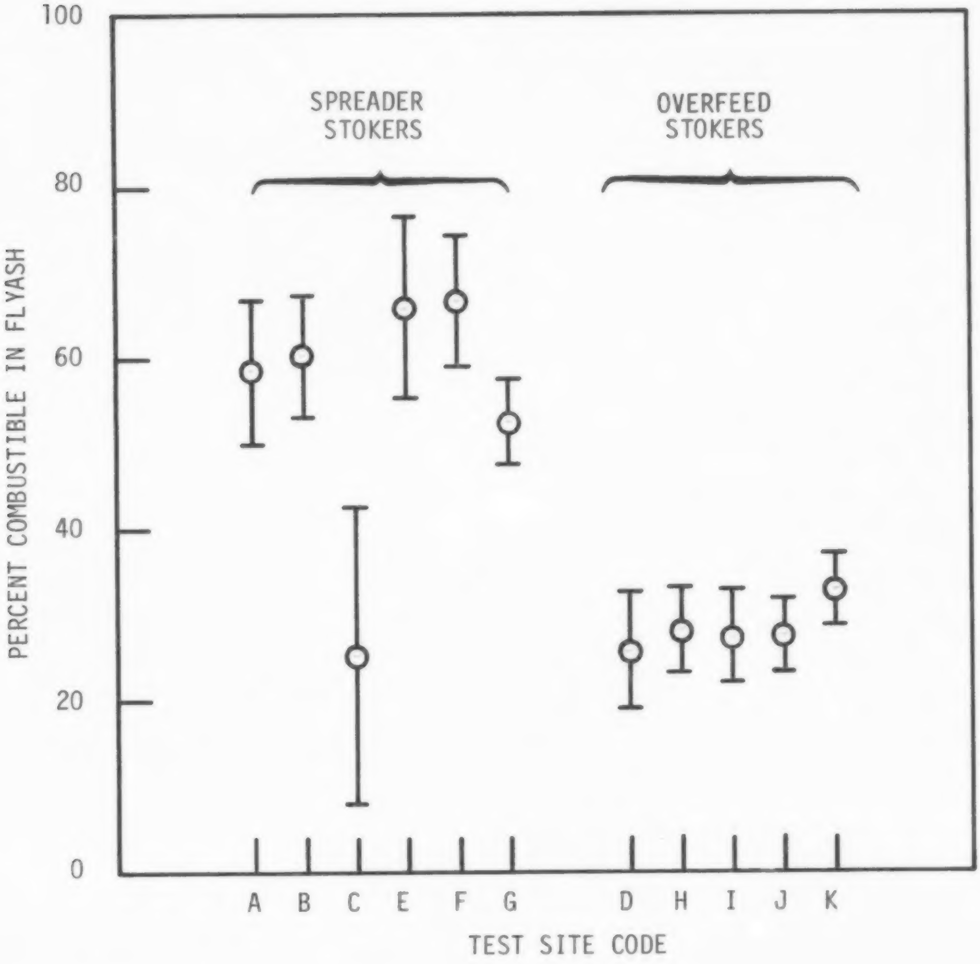

Figure 4. The Average and Standard Deviation of the Mass Percentage of Combustible Material in the Un-Controlled Flyash of Eleven Stoker Boilers.

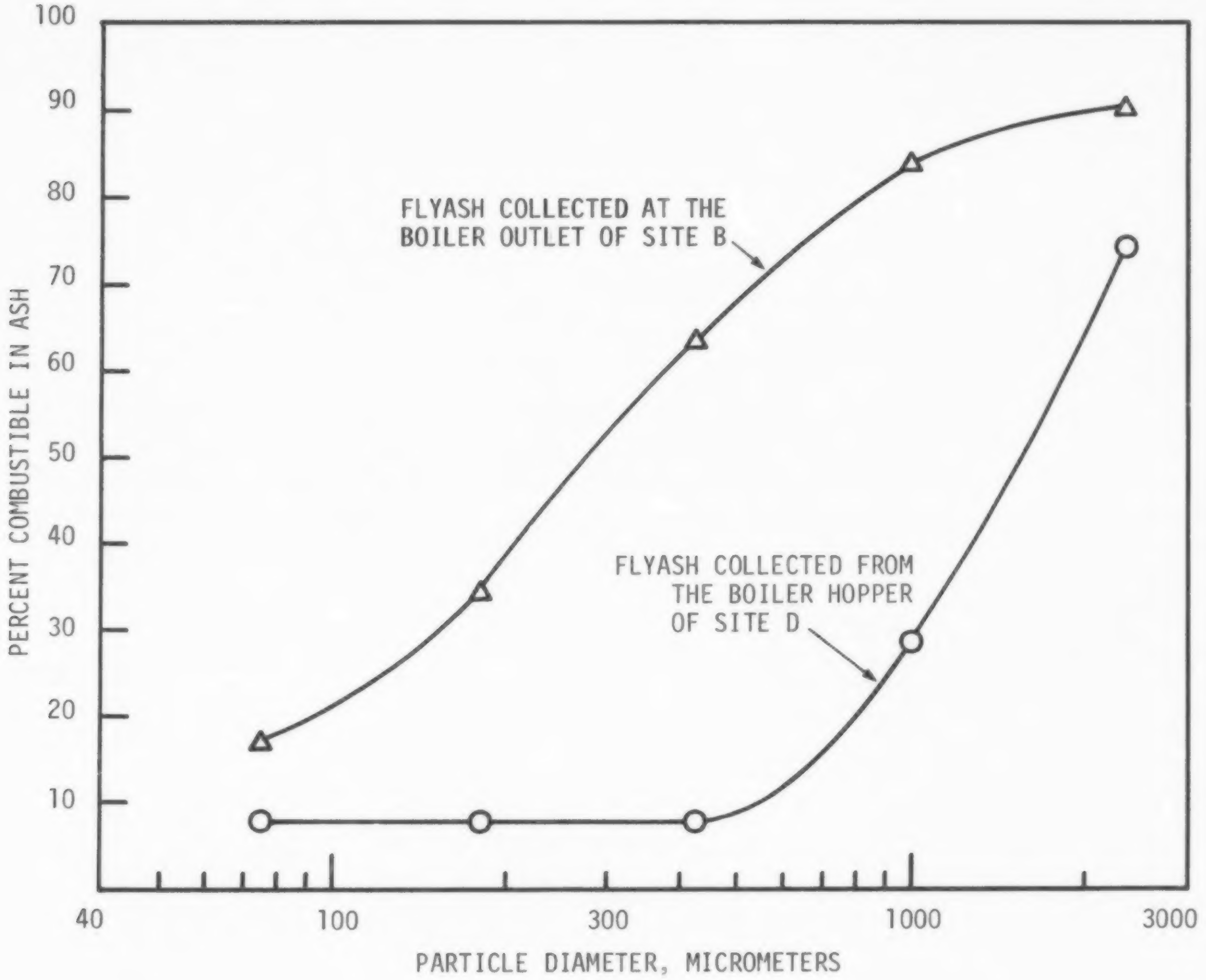

Figure 5. Relationship Between Particle Size and Combustible Content of Flyash from Two Boilers.

COMBUSTION MODIFICATION FOR COAL-FIRED STOKER BOILERS

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ABSTRACT

Preliminary results from a program to develop and assess advanced combustion modification concepts for coal-fired stoker boilers are presented. Tests on a 100,000-lb/hr steam spreader stoker boiler showed that overfire air reduces smoke emissions only when injected in a zone extending a few feet above the fuel bed. Improved overfire air design can permit lower excess O_2 firing for NO_x control, while maintaining acceptable smoke and CO emissions. Staged combustion was applied to a laboratory underfeed stoker (~240,000 Btu/hr heat input) to reduce NO_x emissions.

ACKNOWLEDGMENTS

The authors would like to thank program monitor John H. Wasser of EPA's Combustion Research Branch for his assistance and guidance. They would also like to extend their appreciation to Jim Maloney of the State of Wisconsin and Stan Novotny of the University of Wisconsin for their help in arranging and performing the field tests.

SECTION 1

INTRODUCTION

The restricted availability of natural gas and oil fuel has resulted in the increased use of coal-fired stoker boilers for industrial applications. However, the widespread use of stokers could be limited by environmental constraints if methods are not developed to reduce their emissions. This situation has created the need for a stoker emissions technology program that will develop combustion modification methods for minimizing stoker gaseous emissions, characterize the influence of these modifications on particulate properties which are important in collector design and optimization, and assess the ability of new stokers to comply with present and anticipated pollution regulations. There also is a need for close coordination of this technology development with the stoker industry to maximize technology transfer.

EPA has funded such a program, under EPA Contract No. 68-02-3166, "Application and Assessment of Combustion Modification Concepts for Full-Scale Stoker Coal-Fired Boilers." The major objectives of this recently-begun program are listed below:

1. Establish combustion modification techniques that are practical and effective on a stoker boiler.
2. Characterize the dependence of particulate and other emissions on coal type, coal size, ash reinjection rate, degree of overfire air, load, excess O_2, etc.
3. Determine to what degree the "optimized" stoker emissions are dependent upon coal type.

4. Examine the relationship between stoker design and emissions and determine what latitude exists in burning other than the "design" coal in existing field units.

5. Establish desirable coal characteristics and the requirements for practical use by stokers.

6. Examine the feasibility of burning cleaned or processed coals.

7. Perform Level I emission assessment of stoker-fired boilers, with Level II assessment as necessary.

8. Determine the impact of modified combustion techniques on fly ash collector efficiency and design.

9. Assess the potential for emissions control and overall environmental acceptability of industrial stoker boilers.

10. Prepare a guideline document for use in the industrial and commercial application of successful combustion modification concepts.

Phase I of the program involves tests on two industrial-sized spreader stokers (100,000 and 300,000 lb/hr steam). Testing on the smaller unit is underway and is described in Section 2. When testing on the larger unit is completed, the results will be examined to see how well the various modification techniques scale up.

Three institutional-size moving grate and underfeed stokers will be tested in Phase II. Testing of the first underfeed stoker is currently underway in KVB's laboratory and is discussed in Section 3. This unit will also be used for small-scale tests on advanced combustion concepts that will be used on the larger boilers in the program if successful. The results from each phase will be reviewed by EPA and a technology transfer committee, consisting of representatives from the coal and stoker industries, to decide whether the study has established significant improvements in environmental status for each class of stoker. If so, KVB will prepare a guideline document that will detail the methods and procedures for application of the successful combustion modification concepts.

Some of the combustion modifications to be considered are:

1. Low excess air (LEA) firing
2. Steam injection through overfire air (OFA) jets
3. Undergrate air humidification
4. Undergrate air redistribution
5. Improved OFA addition
6. Addition of recycled flue gas through OFA jets
7. Biased bed loading
8. Clean coal firing

Throughout the study, the results will be evaluated with respect to these questions:

1. How dependent are stoker emissions on the coal type, stoker design, stoker size, and operating parameters?
2. What coal characteristics are desirable for stoker fuel use, and what alternative reconstituted and processed coals are suitable for significantly reducing pollutants?
3. What combustion modifications are practical and effective on a stoker boiler, and what methods are best?
4. How boiler-design-dependent are stoker emissions, and what latitude exists in burning other than the "design" coal?
5. How can coal size, ash reinjection rate, and overfire air configuration be optimized to minimize emissions?
6. What are the trade-offs between emissions and boiler performance for key design parameters?
7. How dependent are particulate size and loading on combustion parameters or combustion modification method, and how do these affect collector design?
8. Are POM, PCB, and other organic emissions significant from fuel-rich stoker beds?
9. What trace elements and other pollutants may be of concern based on Level I and limited Level II screening tests? To what degree are they influenced by combustion modifications?

A key feature of the program is the creation of an industrial technical panel, mentioned above, to review program progress and provide practical advice on technical objectives. Panel members will be drawn from stoker manufacturers, the coal industry, and plant managers at the respective test sites. This panel will help the stoker industry make better use of new design information generated during the study.

This paper presents preliminary results from the field and laboratory investigations, which have just started. In Section 2, the spreader stoker field tests will be discussed. In Section 3, the underfeed laboratory tests will be discussed. Section 4 will summarize the work to date.

SECTION 2

FIELD TESTS

FACILITY DESCRIPTION

Field tests have recently begun on a 100,000-lb/hr steam flow spreader stoker boiler at the University of Wisconsin, Madison, Central Heating Plant. The boiler (Unit No. 1) was constructed by Babcock & Wilcox in 1952, and is fired with three Westinghouse Centrafire spreader stokers with a front-discharge traveling grate, shown in Figure 1. It is a balanced draft unit, firing western Kentucky bituminous coal from the Fies mine. Other specifications are as follows:

- Design pressure - 4.9 MPa (700 psig)
- Steam temperature - 656°K (720°F)
- Actual day-to-day operating pressure - 4.2 MPa (600 psig)
- Boiler heating surface - 131.18 m^2 (1412 sq ft)
- Economizer heating surface - 518.12 m^2 (5577 sq ft)
- Stoker grate size - 4.038 m x 4.94 m (13' 3" x 16' 2-1/2")
- Stoker grate area - 19.96 m^2 (214.8 sq ft)

Overfire air is supplied by a separate fan and injected at a pressure of 16 inches H_2O through three banks of 13 nozzles, each 1.5 inches in diameter. The lower rear bank is about one foot above the grate; the upper rear bank is about 4.5 feet above the grate, directed about 15° down from the horizontal; and the front bank is about two feet above the grate, just below the stokers.

A mobile laboratory has been constructed for the emissions analysis. This laboratory is housed in a 45-foot semi-trailer and includes the following instrumentation:

- NO/NO_x -- Teco Model 10A
- O_2 -- Beckman Model F3M3-1AA
- CO, CO_2 -- Beckman Models 315B
- SO_2 -- Dupont Model 400
- HC -- Carle Model 211 GC.

In addition, the laboratory contains auxiliary equipment to support EPA Method 5 and SASS sampling.

TEST RESULTS

During the tests described here, the fuel burned was not the normal Fies coal but a mixture of the Fies coal and other coal bought 10 years ago during a mine strike. Due to weathering and a recent fire in the coal pile, the coal was much higher in fines than normal stoker coal, precluding full-load operation. These factors limited the testing to the examination, described below, of the effectiveness of overfire air.

To assess the effect of the individual OFA banks, each bank was turned off separately and in combination with other banks. Smoke was monitored with the plant's optical opacity meter. (Each of the five units in this plant has its own opacity meter.)

The result was a dramatic demonstration of the effectiveness of the lower rear OFA bank. Any combination of active banks including the lower rear kept the opacity below five percent, while any combination without air through the lower rear OFA jets resulted in opacities of 45 percent or greater.

DISCUSSION

These results seem to indicate that the OFA is effective only within a region a few feet above the bed, as the front and upper rear OFA jets are two and five feet above the grate. The rising combustion products keep the air jet from penetrating across the grate.

It is interesting that one bank of jets on the back wall should have such a profound effect on smoke emissions since viscous flow theory predicts that the centerline jet velocity will decrease to less than 20 percent of its original value within 30 nozzle diameters. For the Madison unit, 30 nozzle diameters is just 3.75 feet. Thus, the rear OFA jets would appear to cover less than 25 percent of the grate area before their velocity diminishes to insignificance. Yet this is enough to make the difference between a clean stack and opacities of 45 percent or greater.

Two engineers entered the furnace of a twin unit, down at the time, to get an idea of how quickly the OFA velocity decayed. They found that the jet velocity had diminished to a barely-discernible breeze four feet from the nozzles. Turning off two banks increased the velocity of the remaining bank slightly, but had no measurable effect on the penetration distance.

FUTURE TESTS

A modified OFA system is currently being constructed. It will consist of three tubes mounted crosswise across and roughly two feet above the grate, drilled with holes similar to the existing OFA jets. These invasion pipes will be almost evenly spaced (they will be inserted through observation hatches) and should cover the grate much better than the existing OFA system. The significance of improved OFA with respect to NO_x reduction is the possibility of reducing excess air while retaining acceptable CO and smoke levels. Steam injection will also be tried with the invasion pipes. The steam should improve carbon burn-out as well as provide improved mixing.

Another test currently underway is examining whether combustion is uniform over the grate. Eight probes have been installed at the boiler exit plane, and gas samples from these probes will be used to spot regions of abnormal CO or O_2 on the bed, assuming essentially laminar flow through the boiler. The results can be used to balance the three stokers to achieve more uniform combustion conditions.

SECTION 3

FACILITY DESCRIPTION

FACILITY DESCRIPTION

To provide a small-scale test bed for advanced combustion modification concepts and new fuel evaluations, a single-retort underfeed stoker burner was constructed in KVB's Santa Ana laboratory. The unit was designed to be as versatile as possible and burns about 20 lb coal/hr (about 240,000 Btu/hr heat input). A schematic of the stoker is shown in Figure 2; it is equipped with a lower overfire air torus, comparable to normal overfire air on a full-scale stoker, and a variable-height upper overfire air torus for staged combustion concept tests. Recycled flue gas can be mixed with the overfire air, and different mixtures can be injected in each torus. Steam (50 psig) can also be injected in each torus and in the undergrate air.

The firebox is lined with refractory. (Removable boiler tubes have also been fabricated to vary the radiant section's heat removal rate, but these were not used in the experiments described here.) The flue gas is cooled by a water-jacketed convective section. Flue gas can be recycled from both before and after the convective section and mixed to control the temperature of the recycled flue gas.

Emissions of NO, NO_x, SO_2, CO, CO_2, O_2, and smoke are monitored by the laboratory's instrumentation system, which has been described elsewhere.* For the tests described here, smoke was measured with a Bacharach pump and reported on the Bacharach oil scale while an optical opacity meter was being installed.

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*Muzio, L. J., J. K. Arand, and K. L. Maloney, "Noncatalytic NO_x Removal with Ammonia," EPRI Report FP-735, April, 1978.

TESTS

In the first tests, the height of the upper air torus was varied over its full range (0 to 34 inches above the coal bed) to examine the effect on NO emissions. Kentucky bituminous coal was the fuel (the coal analysis is shown in Table I), and no flue gas was added to either overfire air stream. In the unmodified baseline condition the NO_x emissions were in good agreement with the field test results from the Madison boiler at 350 ppm.

With an upper/lower overfire air flow ratio of 2, the NO_x emissions were minimized at 176 ppm (3% O_2, dry) when the torus was 28 inches above the grate. NO_x emissions peaked at 394 ppm when the torus was 12 inches above the bed. As shown in Figure 3, the O_2 roughly followed the NO_x curve, peaking at 10 percent with the torus 8 inches above the bed. The variation in O_2 was attributed to changing bed conditions. It was noted that clinker formation caused the O_2 to rise one or two percent at otherwise steady conditions.

Carbon monoxide and smoke readings are shown with O_2 in Figure 4. The CO rose slightly as the upper torus was moved from directly above the lower torus to 20 inches above the bed. The CO then rose quickly from about 90 ppm (3% O_2, dry) to 350 ppm at the highest torus setting. At the lowest NO_x point, the CO was a still-reasonable 150 ppm. The smoke posed a problem, however. In the low-NO_x range, the smoke number was above 8 on the Bacharach oil scale. At the lower torus settings, the smoke number was highly variable, jumping back and forth between 2.5 and 9. This was felt to be a bed effect; the addition of a continuous opacity monitor should provide insight as to the relation between bed condition and smoke emissions.

DISCUSSION

The effectiveness of staged combustion in reducing NO emissions can be seen by comparing Figure 3 with Figure 5. Figure 5 shows NO emissions vs O_2 without staging (i.e., only the lower OFA torus was activated). Reducing the O_2 from 10 percent to 6 percent reduced the NO by 25 percent. From Figure 3, the same change in O_2 reduces the NO_x by 50 percent. (In Figure 3, the NO_2 generally ranged from 0 to 15 ppm). The unstaged tests were run burning a low sulfur western subbituminous coal; however, the NO emissions are similar for the unstaged point in Figure 3 (i.e., the point at which the upper torus is directly above the lower torus) and the comparable point in Figure 5.

An interesting, and unresolved, question is: why does the NO_x peak as the upper torus is raised?

For these tests, accurate measurements of the undergrate air or coal flow were not available, so it was not possible to calculate fuel/air ratios in the different stages. Future tests will provide this information.

This work will continue with tests of steam and recycled flue gas in the OFA jets, comparison of eastern and western coals, and specie and temperature mapping to analyze the staging process.

SECTION 4

SUMMARY AND CONCLUSIONS

Preliminary studies have been performed to date on a 100,000-lb/hr steam flow spreader stoker boiler and a 240,000-Btu(t)/hr underfeed stoker furnace. The effectiveness of the various sets of overfire air jets on the spreader stoker has been investigated, and staged combustion has been implemented on the underfeed stoker.

These tentative conclusions have been drawn:

1. The effectiveness of overfire air jets seems confined to a zone extending only two or three feet above the fuel bed. This indicates that currently used overfire air flow rates may be excessive and that lower excess air firing for NO_x control can be achieved by optimized OFA design.

2. Staged combustion can be an effective technique for lowering NO_x emissions. The major contribution to NO_x emission is fuel nitrogen; running the coal bed more fuel-rich inhibits conversion of fuel N to NO_x.

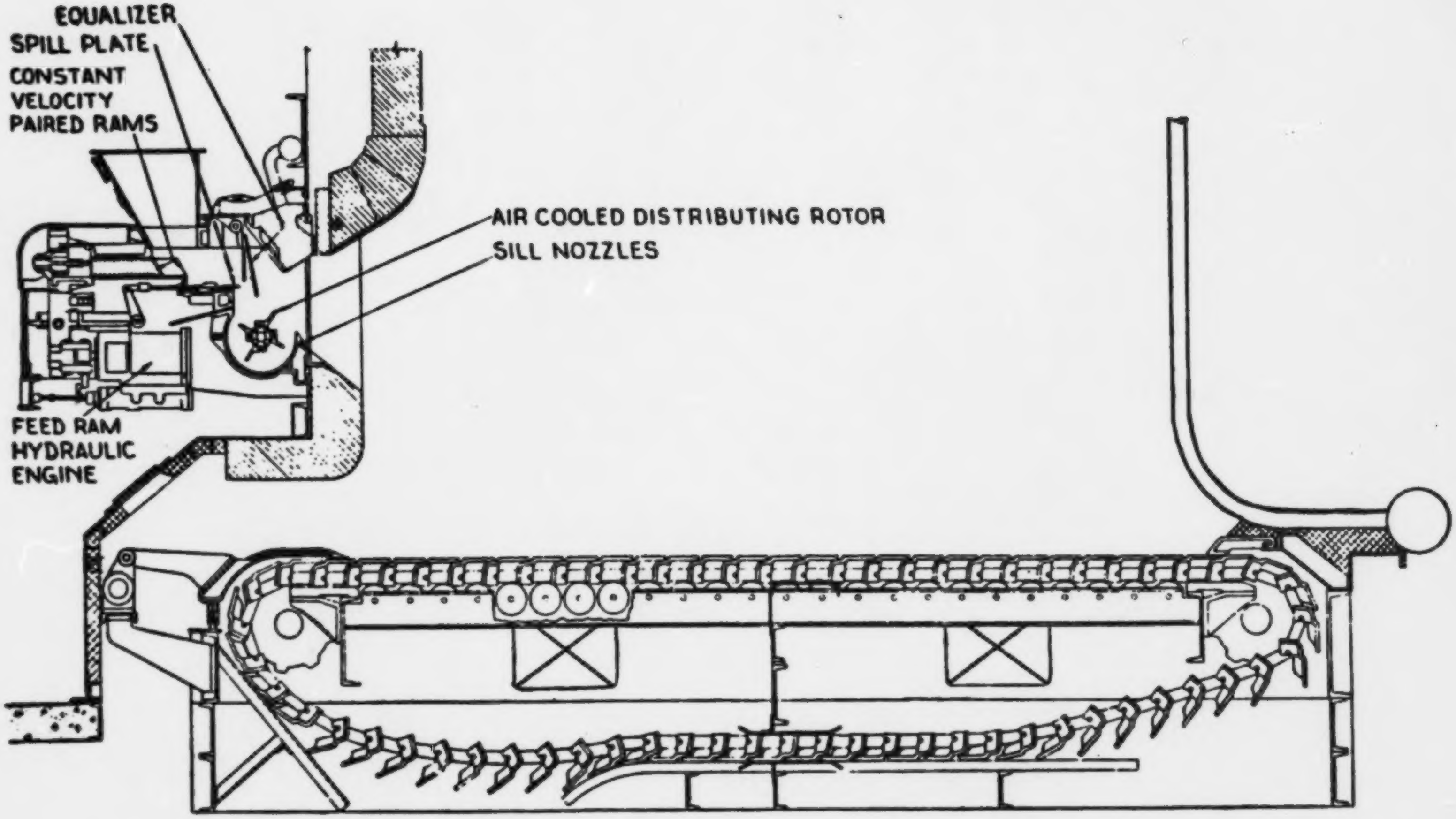
EQUALIZER
SPILL PLATE
CONSTANT VELOCITY PAIRED RAMS
AIR COOLED DISTRIBUTING ROTOR
SILL NOZZLES
FEED RAM HYDRAULIC ENGINE

Figure 1. Westinghouse Centrafire spreader stoker with traveling grate.

TABLE I. COAL PROPERTIES - KENTUCKY BITUMINOUS

Proximate Analysis	
% Moisture	3.85
% Ash	8.97
% Volatile	36.31
% Fixed Carbon	50.87
HHV (Btu/lb)	12,698
Ultimate Analysis (% wt)	
Moisture	3.85
Carbon	71.31
Hydrogen	4.79
Nitrogen	1.29
Sulfur	1.01
Ash	8.97
Oxygen	8.74

THIRTY-DAY FIELD TESTS OF INDUSTRIAL BOILER COMBUSTION MODIFICATIONS

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ABSTRACT

This paper is based on a field test program sponsored by EPA to evaluate the long-term effectiveness of combustion modifications for reducing NO_x emissions from industrial boilers. Five 30-day field tests have been conducted so far. The combustion modifications evaluated include low excess air on a coal-fired spreader stoker, staged combustion air on a residual-oil-fired boiler, staged combustion air and staged combustion on a pulverized-coal-fired boiler, low excess air and staged combustion air on a spreader stoker, and a gas-fired low NO_x burner. Reductions in NO_x varied from 15 percent with the pulverized-coal-fired boiler to approximately 70 percent with the gas-fired low NO_x burners. No serious operational or reliability problems were encountered, and most units demonstrated an increase in boiler efficiency.

THIRTY-DAY FIELD TESTS OF INDUSTRIAL BOILER COMBUSTION MODIFICATIONS

INTRODUCTION

A field test program is being sponsored by EPA's Combustion Research Branch and their Office of Air Quality Planning and Standards to determine whether combustion modification techniques which demonstrated reductions on air pollutant emissions (particularly oxides of nitrogen) during short-duration tests are feasible over longer periods. In addition, boiler performance and reliability are being monitored. KVB, Inc., was selected to conduct this field test program with the purpose of providing data to be used by EPA in the preparation of a new source performance standard for NO_x emissions from industrial boilers.

The program scope requires testing of seven industrial boilers ranging in capacity from 50,000 to 250,000 lb steam/hr. Fuels include natural gas, distillate and residual oil, and coal. NO_x control technologies to be evaluated are low excess air, staged combustion air, low NO_x burners, and flue gas recirculation.

Continuous measurements of gaseous emissions (NO, CO, CO_2 and O_2) were made with a certified monitor fabricated by KVB. Particulate emissions were measured in accordance with EPA Reference Method 5.

Five 30-day field tests have been completed. Equipment tested includes two spreader stokers, a pulverized-coal-fired boiler, a residual-oil-fired boiler, and a natural-gas-fired boiler.

TEST PROCEDURES

The NSPS for industrial boilers may include emissions standards averaged over a time period as long as 24 hours. A source testing program will be more supportive of the standard if it utilizes techniques which acquire data over a long time period or continuously.

The accepted EPA Reference Methods for determining the emission rates of particulate and NO_x are Methods 5 and 7, respectively. Each of these methods extracts pollutant samples over a short time period. Method 5 will extract a sample for 60 minutes. Method 7 will extract a sample in less than a minute. These methods result in source emission rates that are averaged over short time periods. A measurement of emission rates averaged over longer time periods had to be obtained in the past by conducting multiple Reference Method tests. For gaseous pollutants, this approach can be improved upon by utilizing the continuous monitoring system methodology.

Using a continuous monitoring system (CMS) to collect data in support of a standard will be more defensible if those data can be correlated with an EPA Reference Method. The mechanism for doing this is provided within Performance Specification 2 (PS2), 40 CFR 60, Appendix B. In PS2 criteria are set for installing and testing a NO_x or SO_2 continuous monitoring system. PS2 also establishes minimum performance specifications that the system must meet in terms of eight parameters: accuracy, calibration error, 2- and 24-hour zero drifts, 2- and 24-hour calibration drifts, response time, and operational period. The accuracy (relative) parameter compares data from the CMS to data obtained via an EPA Reference Method test. CMS and Reference Method tests are run simultaneously, with at least 27 tests for NO_x being run. The accuracy is the mean difference of the two measurement techniques plus a 95 percent confidence interval. This value must be within 20 percent of the EPA Reference Method. Therefore, each performance evaluation of a CMS conducted according to PS2 serves the dual purpose of insuring that the equipment is operating properly and providing a means for correlating the data with an EPA Reference Method.

The data collected from a continuous monitoring system over a 30-day test period should adequately represent the emission rate that would have been derived from Reference Method testing if the following criteria are met:

1. The CMS is installed in accordance with Performance Specification 2.
2. The CMS passes a complete performance evaluation at the beginning of the test period.
3. The CMS passes the relative accuracy portion of the performance evaluation at the end of the 30-day test period.

This assumes that daily span gas checks are performed and that there are no replacements of major components.

General

All boiler operating conditions were recorded including fuel feed rate, steam production rate, and excess oxygen. This was done via hourly operation logs and periodic recordings by a technician on site.

The nitrogen (N), sulfur (S), and ash contents, as well as heating value, were determined for oil and coal samples. For coal, the state, county, bed, seam, and mine from which the coal was obtained were provided.

Because of coal nitrogen and sulfur variability, coal samples were collected periodically during the day and composited into a single sample for analysis. Sample collection and size reduction were conducted according to American Society of Testing and Materials methods. Samples were analyzed periodically for ultimate analysis, ash analysis, ash fusion temperature, and any other properties which may be essential to boiler performance evaluation.

For oil, the number of samples analyzed was significantly lower. Analyses were necessary only to characterize each batch (tankful) of fuel burned. The American Petroleum Institute gravity of the oil samples was also determined. All testing included monitoring for CO_2 and O_2 so that the data collected on particulate and NO_x could be converted to any of the possible units of a standard. Visible emission readings (Reference Method 9, 40 CFR 60 Appendix A) were taken at least every time a Method 5 or 7 was performed. When particulate source testing was performed, a Method 9 was completed as often as was reasonable considering manpower and plume variability. One set of measurements for polycyclic organic matter was obtained.

Particulate Testing

There are no EPA performance specifications for continuous particulate monitoring equipment. Therefore, particulate testing was performed by repetition of Reference Method 5. Each day's testing consisted of triplicate runs of the Reference Method. Initially three triplicate runs, a total of 9 Method 5's, were conducted. The triplicate sets were conducted at the start, midpoint, and conclusion of the 30-day test. After the second test site, it was decided to drop the triplicate series at the midpoint of the 30 days because of the cost involved. Particulate testing was not conducted at the gas-fired boiler test site.

Gaseous Pollutants (NO_x and CO)

A continuous monitor system which met PS2 and PS3 specifications was used as the source test method for NO_x and CO. The source tests consisted of 30 days of continuous monitoring. The NO_x control technologies employed consisted of combustion modifications which allow for a single monitoring point.

Complete PS2 and 3 tests were performed at the beginning of each 30-day test period. The relative accuracy portion of the performance evaluation was repeated at the end of the 30-day test period. In addition, an abbreviated relative accuracy test, consisting of PDS flasks, was conducted at the midpoint of the 30-day test. A chronology of a typical 30-day test is shown in Figure 1.

Instrumentation

The continuous monitor shown in Figure 2 was equipped with analytical instruments to measure concentrations of NO, CO, CO_2, and O_2. Gaseous measurements were made with the analytical instruments listed in Table I. The sample gas is delivered to the analyzers at the proper condition and flow rate through a sampling and conditioning system. A stainless steel probe and sintered stainless steel filter were installed in the stack to sample the flue gas. The CMS is equipped with three two-pen strip chart recorders for continuous recording of gaseous concentrations. A 20-channel automatic data logger was later added to reduce the data reduction task.

IMPLEMENTATION OF LOW NO_x OPERATING MODE

One area of concern in the implementation of a low NO_x operating mode is how to preserve a low emission level for extended duration through routine maintenance. A number of visual observations and supporting measurements are available to confirm the performance after combustion modification. The items listed in Table I may be useful as a checklist on NO control combustion performance.

Visual observations are important, even in coal-fired units, to detect possible flame impingement, stability, or slagging and fouling problems. Staged combustion tends to result in longer flames that, if not properly controlled, can lead to flame impingement, slagging, and tube corrosion in the lower furnace region. Excess O_2 control and flame stability are critical. They are influenced by combustion uniformity across the burner region, careful maintenance of burner parts, and bulk gas motion due to inter-burner mixing. Uniformity of burner mixing and completeness of combustion should be confirmed by gaseous emissions traverses in the exhaust duct. Local gaseous emission measurements in the lower furnace region through modified viewing or service ports may be desirable to establish that local reducing atmospheres that could lead to tube corrosion are not present.

Satisfactory implementation of a low NO_x mode for the long term is very strongly dependent on a number of critical factors in individual boiler design and maintenance. Almost any design factor or maintenance item that can affect the performance of the fuel or combustion air system is critical to the delicate balance of combustion conditions necessary for low NO_x. A number of important design limitations may be encountered that compromise or make combustion modifications more difficult. Table II lists some of these factors, such as the mill or primary air capacity, which may limit the number of BOOS or the burner pattern.

The preservation of low NO_x emissions requires careful attention to a number of critical maintenance items, mostly associated with the fuel and combustion air systems.

TEST RESULTS

Five of the planned seven 30-day tests have been completed and final reports written. The five test sites include two spreader stokers, a pulverized-coal-fired unit, a residual oil-fired boiler, and a natural gas-fired boiler. The results of the tests are summarized in this section.

Site 1, Coal-Fired Spreader Stoker

Site 1 was a 100,000-lb steam/hr coal-fired spreader stoker. The NO_x control technology employed on this unit was low excess air (LEA). The LEA condition was maintained for 30 days with a mean NO emission level of 170 ng/J (278 ppm @ 3% O_2, dry) with the boiler load between 20.5 and 23.2 MW thermal output (70,000 to 79,000 lb steam/hr). At the same load, baseline NO emissions are 200 ng/J (360 ppm). A log-probability plot of the NO emissions for the coal-fired spreader is presented in Figure 3.

Site 2, Residual-Oil-Fired Boiler

Site 2 was a 26.4-MW output (90,000 lb steam/hr) residual-oil-fired boiler. The NO_x control technology employed on this unit was staged combustion air (SCA). The as-found concentration of NO_x was 130 ng/J (235 ppm at 3% O_2, dry). Firing in the low NO_x mode, with staged combustion air, resulted in NO_x emission reduction of approximately 23 percent to 100 ng/J (181 ppm at 3% O_2, dry). Staged combustion was accomplished by removing from service the top burner in the triangular arrangement. All air registers were left open. Capacity of the boiler was reduced to approximately 60,000 lb/hr due to fuel pressure limitations. Normally, during low NO_x testing the oil gun tips are changed to allow the boiler to operate at full capacity with burners out of service. At this site, larger tips were not available at the time of the test, so the test was conducted at lower capacity. A log-probability plot of NO emissions is presented in Figure 4 for the boiler operating with SCA. The mean value was 100 ng/J (181 ppm), and 99 percent of the data are less than 130 ng/J (235 ppm).

Site 3, Pulverized-Coal-Fired Boiler

Site 3 was a 76.2-MW (260,000 lb steam/hr) output, pulverized-coal-fired watertube boiler. The NO_x control technology employed on this unit was staged combustion air and low excess air. The results indicate that staged combustion air and low excess air can be effective techniques for NO_x control. However, additional operational problems such as flame stability can be encountered. The baseline NO measurement was 498 ng/J (815 ppm @ 3% O_2, dry) with the unit operating at approximately 70 percent of capacity. At approximately the same load, low NO_x operation yielded a NO emission level of 422 ng/J (691 ppm @ 3% O_2, dry) for a reduction of approximately 15 percent. The average NO emission level for 30 days, firing with staged combustion air and low excess air at loads varying from 15 MW to 63 MW, was 340 ng/J (557 ppm @ 3% O_2, dry). Boiler efficiency showed an increase of approximately 1 percent under low NO_x firing condition. A log-probability plot of the NO emissions is shown in Figure 5 for the boiler. The mean value is 340 ng/J (557 ppm).

Site 4, Coal-Fired Spreader Stoker

Site 4 was a 38.1-MW output (130,000 lb steam/hr) coal-fired spreader stoker. The NO_x control technology employed on this unit was low excess air and staged combustion air. The results indicate that low excess air firing is an effective long-term NO_x control technique for spreader stokers, while the use of staged combustion air by overfire air adjustment is not. The as-found concentration of NO_x was 240 ng/J (409 ppm at 3% O_2, dry) with the boiler load at 80 percent of design capacity. Firing in the low excess air mode resulted in a reduction of approximately 19 percent from the as-found condition. Low excess air firing also resulted in an increase in efficiency of approximately 1.2 percent, and a decrease in particulates of about 22 percent. A log-probablity plot of the NO emissions is shown in Figure 6 for this boiler. The mean value of NO is 211 ng/J (360 ppm) with 99 percent of the values less than 245 ng/J.

Site 5, Gas-Fired Low NO_x Burner

Site 5 was a 24.9-MW (85,000 lb steam/hr) watertube boiler outfitted with low NO_x burners. The 30-day test was conducted with the unit firing natural gas. The mean NO emission level was 33 ng/J, with a geometric dispersion of 1.12 at the high load condition. At low loads (<11 MW) the mean NO emission level was 44 ng/J with geometric dispersion of 1.14. Tests with an adjacent identical boiler with standard burners produced NO emissions of 113 ng/J at boiler loads greater than 11 MW and 95 ng/J at less than 11 MW. A log-probability plot of NO emissions is shown in Figure 7 for the boiler under high load conditions.

CONCLUSIONS

Combustion modification techniques that have demonstrated reduction of air pollutant emissions during short duration tests have been shown to be effective for extended periods.

Little adverse effect on boiler performance or reliability was observed during the five 30-day tests.

The continuous monitor system employing an extractive sampling system provided accurate, reliable data.

Chronology of Typical Source Test

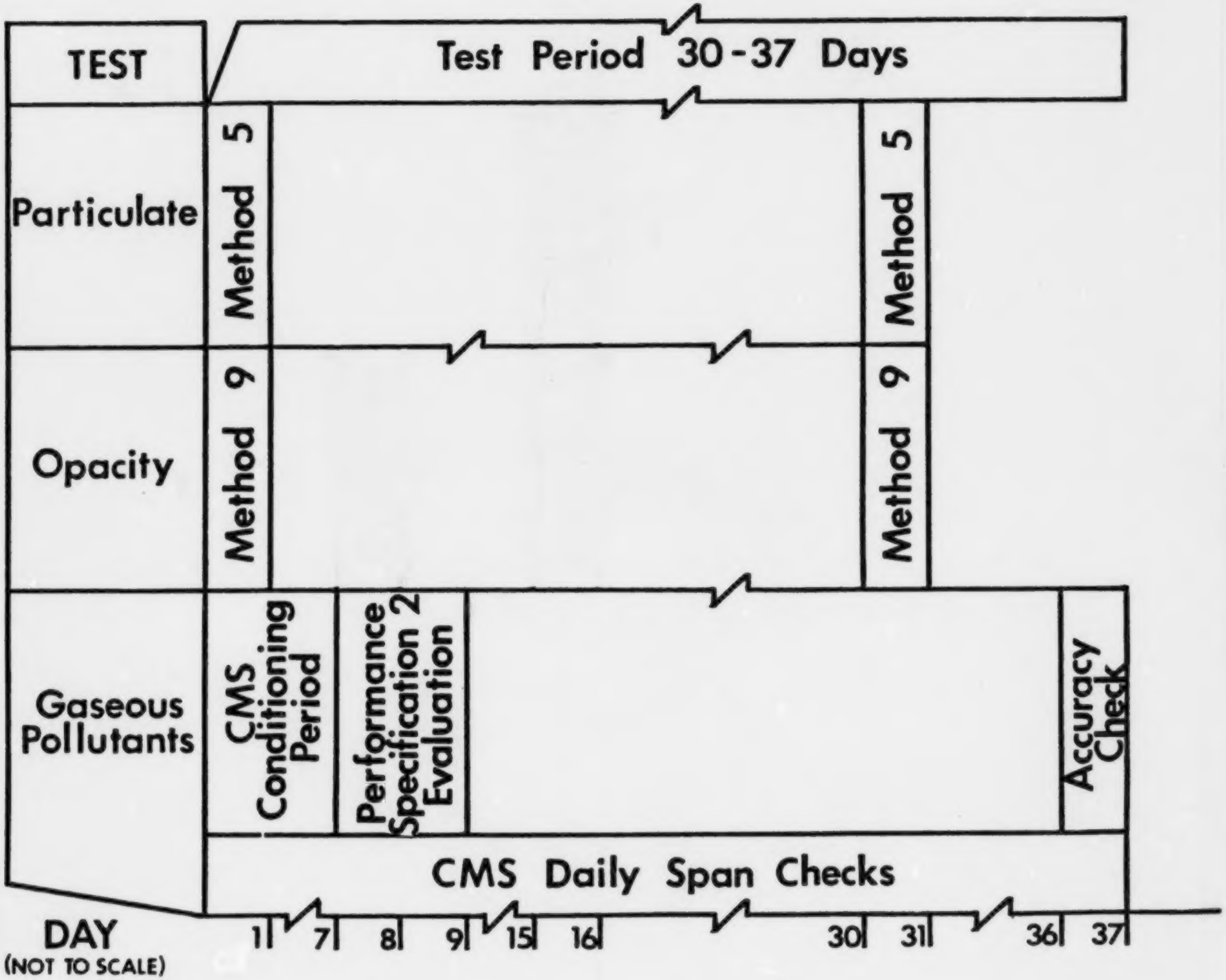
TEST
Test Period 30-37 Days
Particulate
Method 5
Method 5
Opacity
Method 9
Method 9
Gaseous Pollutants
CMS Conditioning Period
Performance Specification 2 Evaluation
Accuracy Check
CMS Daily Span Checks
DAY
(NOT TO SCALE)
1
7
8
9
15
16
30
31
36
37

Figure 1. Chronology of typical source test

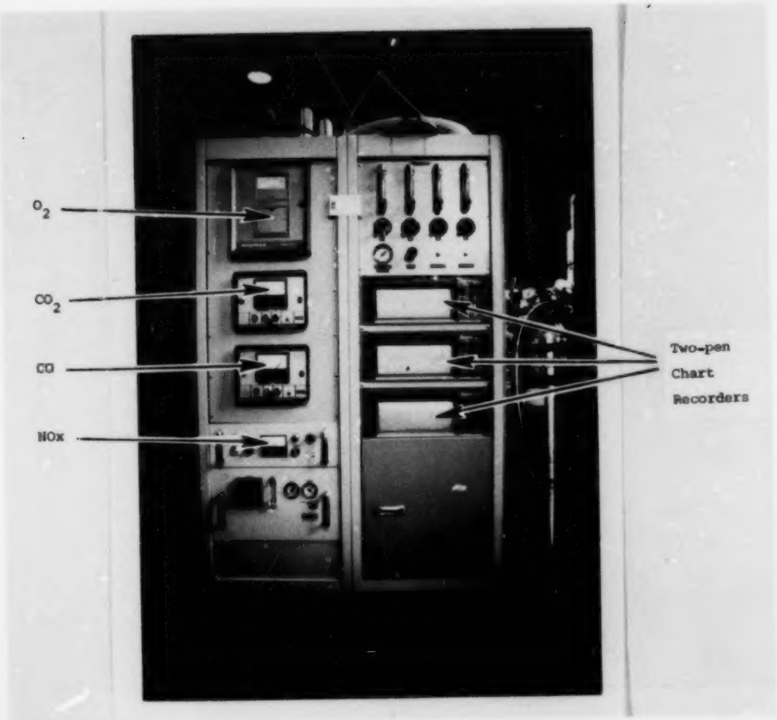
O_2
CO_2
CO
NOx
Two-pen
Chart
Recorders

Figure 2. Continuous monitor.

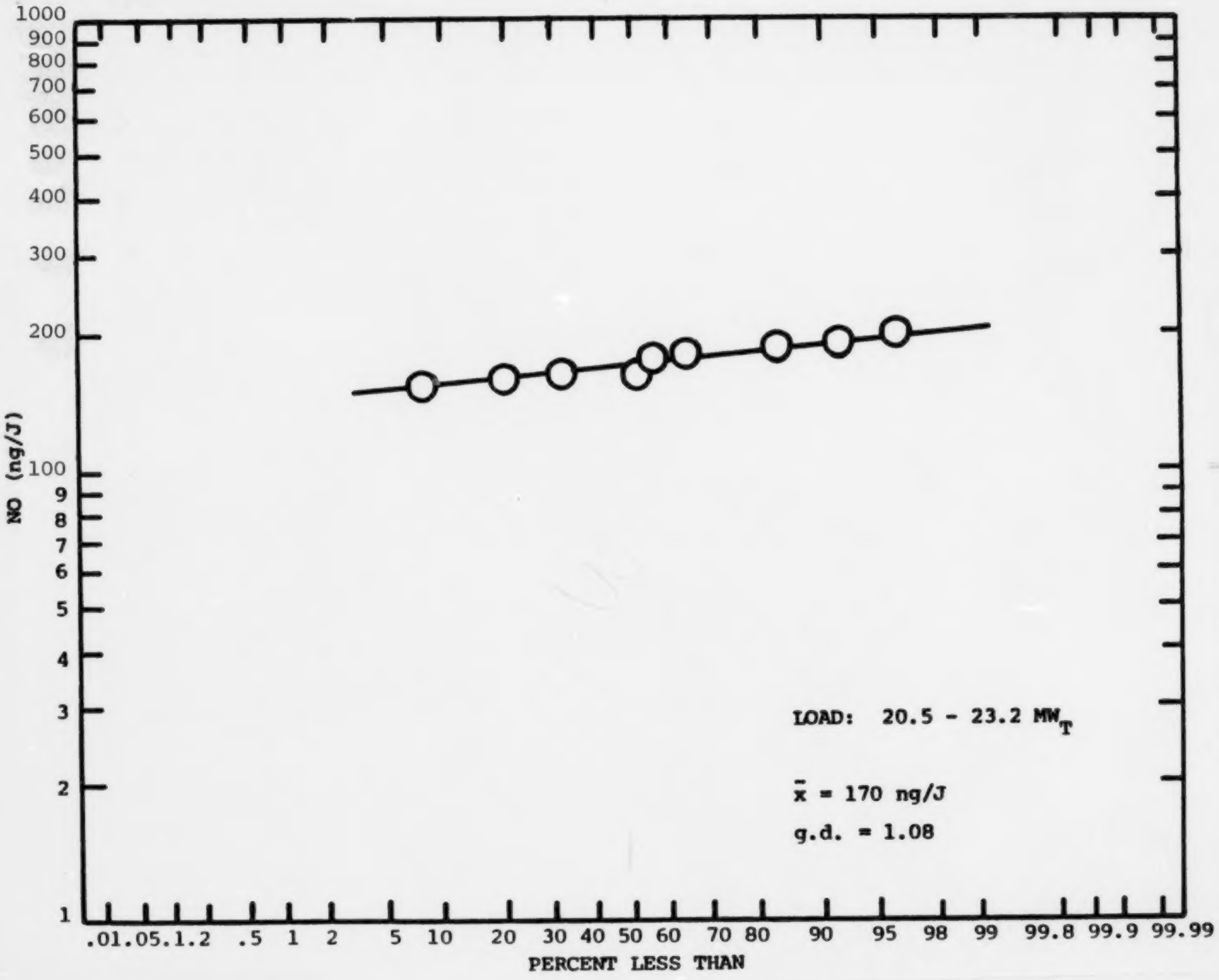

Figure 3. NO emissions from site 1, coal-fired spreader stoker

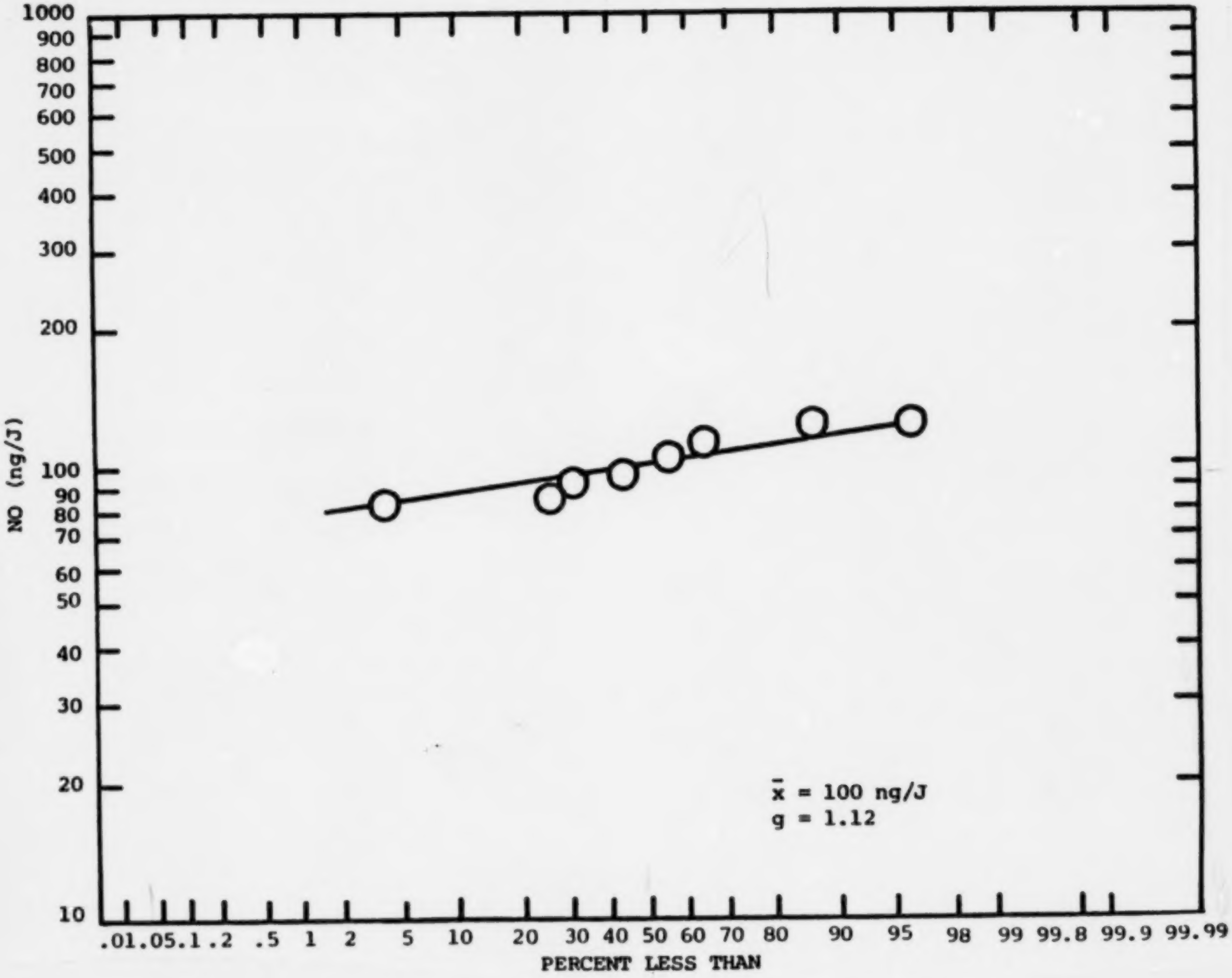

Figure 4. Site 2, residual-oil-fired boiler, staged combustion air (BOOS)

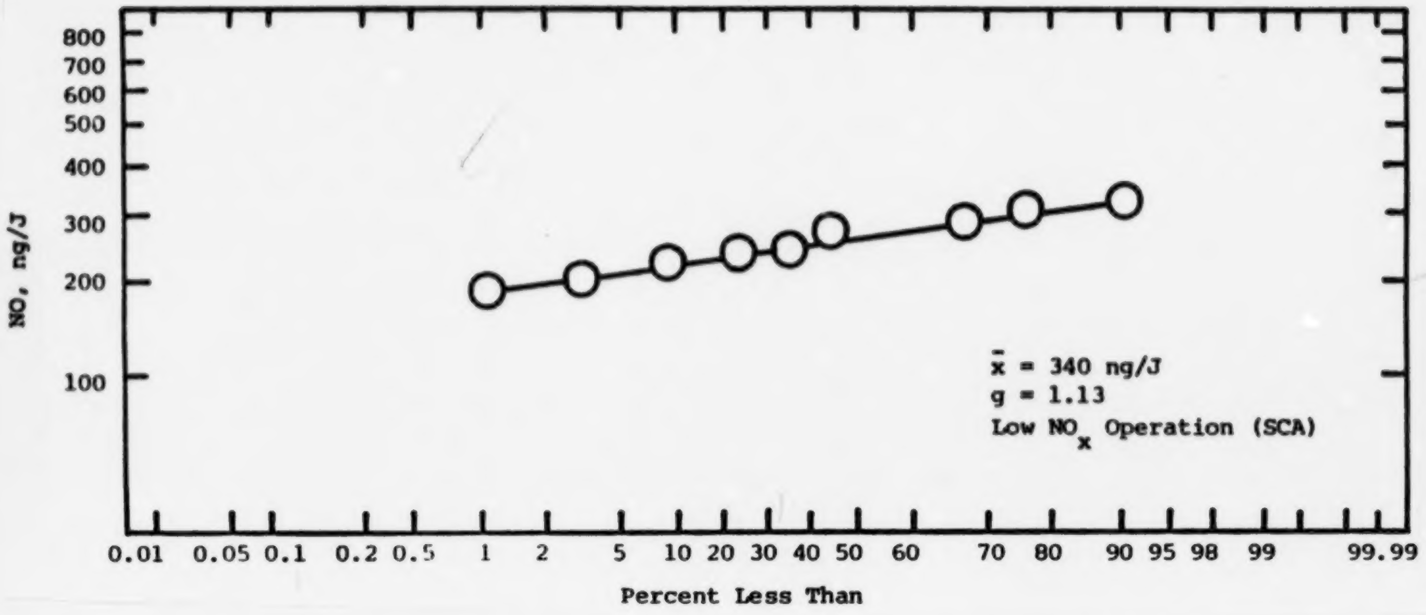

Figure 5. NO emissions from site 3, pulverized-coal-fired boiler

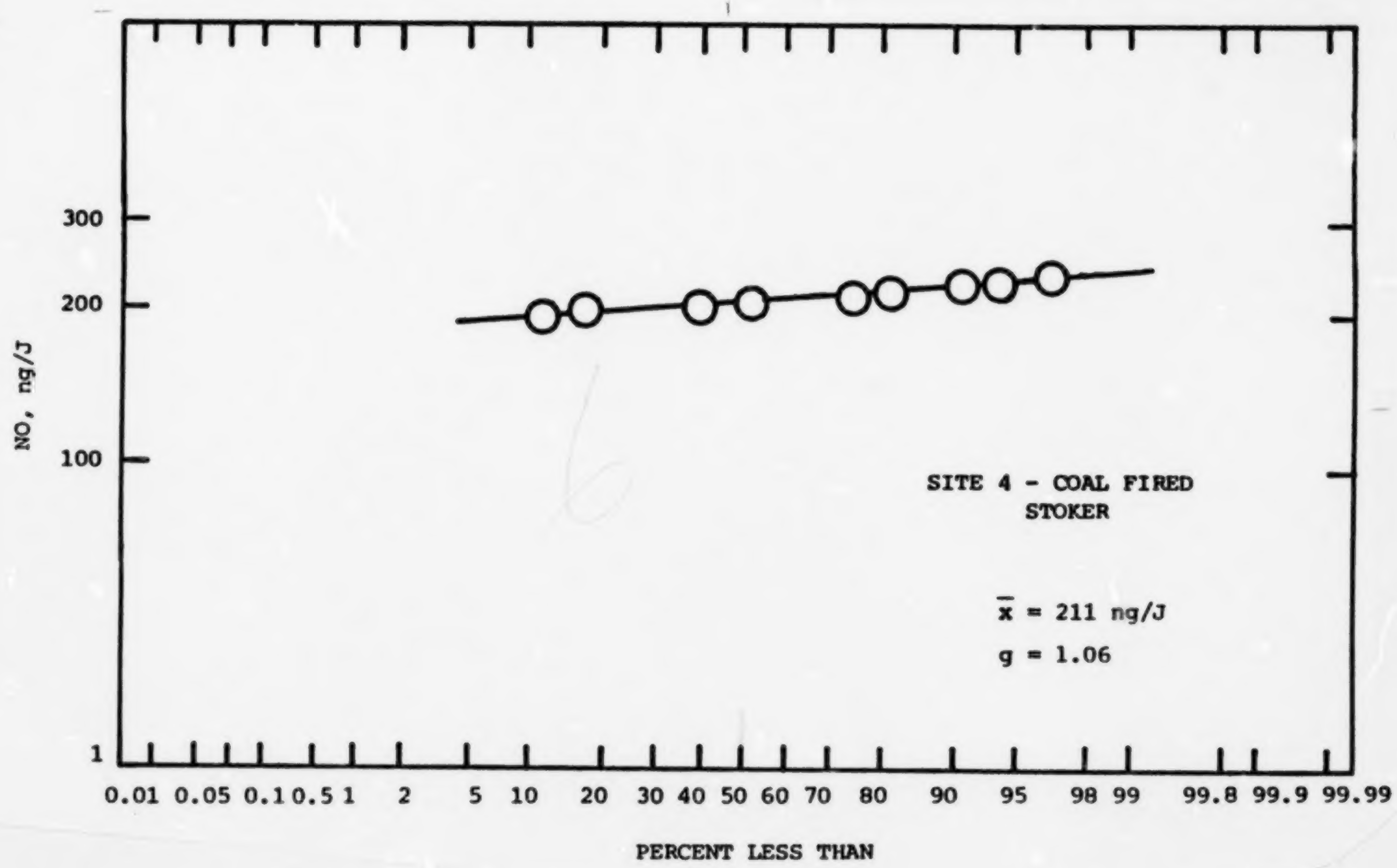

Figure 6. NO emissions from site 4, coal-fired spreader stoker

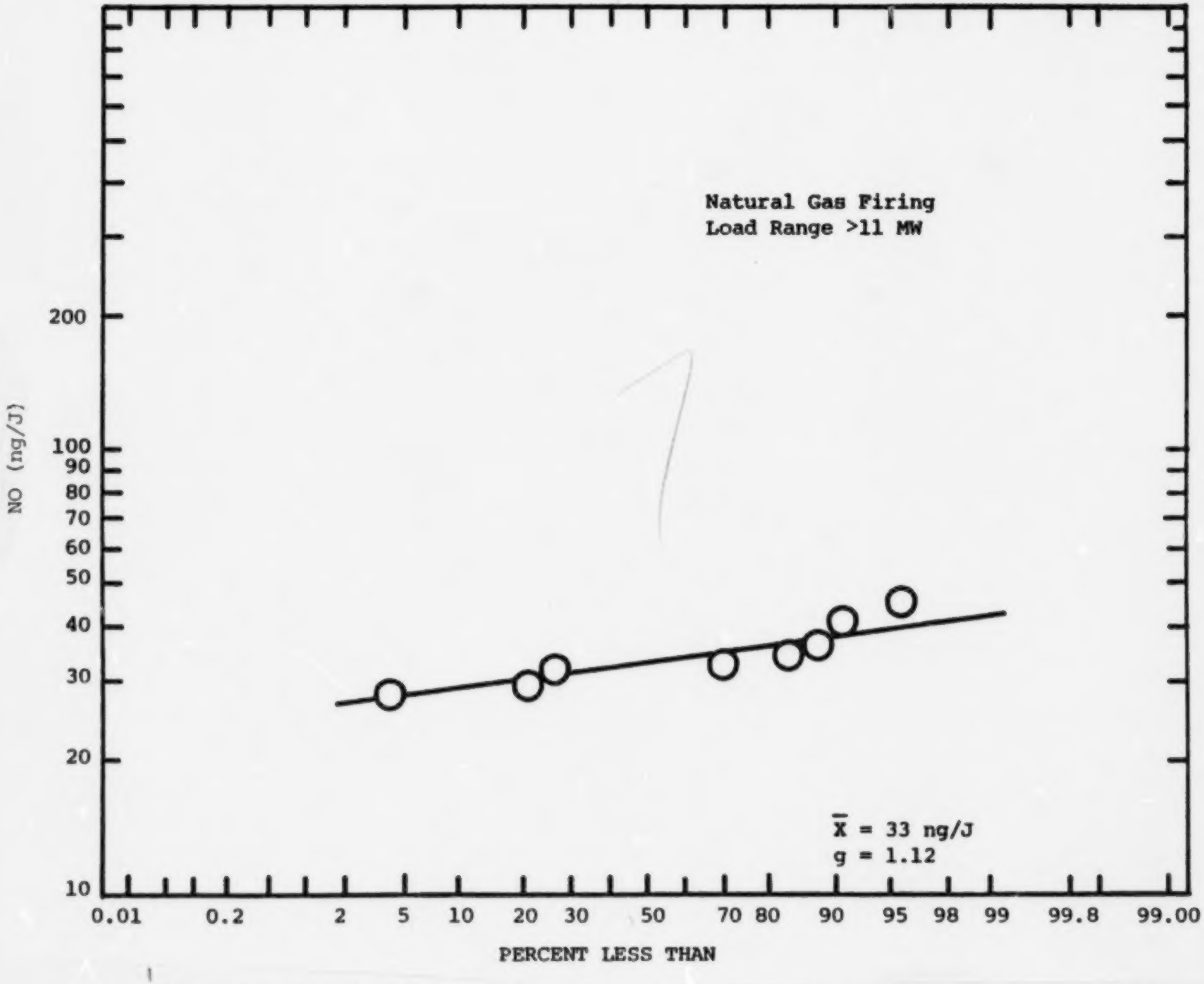

Figure 7. NO emissions from site 5, low NO_x burner/watertube boiler

TABLE I

FACTORS TO CONSIDER IN EVALUATING THE SUITABILITY OF A LOW NO_x FIRING MODE

Visual Observation	Gaseous Emissions Data	Particulate/ Fly Ash Samples	Equipment Operating Data
Flame stability	Combustion balance	Carbon carryover	Tube metal temp.
Slagging/fouling	Burner mixing	Particulates	Steam temperature
Bulk gas motion	Operating O_2 level	Ash characteristics	Firing rate
Combustion uniformity	Potential tube corrosion	Combustion efficiency	Efficiency
Completeness of combustion	Boiler efficiency	Precipitator performance	Pulverizer performance
Flame impingement			Feeder operations
			Auxiliary load
			Burner front settings

TABLE II

OPERATIONAL CONSIDERATIONS IN IMPLEMENTING LOW NO_x COMBUSTION MODIFICATIONS

Boiler Design Factors

Mill/PA capacity, maximum and minimum
Burner pattern/mill arrangement
Coal pipe design and coal distribution
Burner design
Windbox design
Overfire air port configuration/mixing
Excess oxygen sensors, number and placement
CO sensors/instrumentation
Fuel/air flow instrumentation

Critical Maintenance/Adjustment Items

Burner impellers
Pulverizer adjustments/wear, parts replacement
Classifier setting
Primary air control/instrumentation
Coal pipe dams/balance
Feeder balance
Feeder bar height
Mill balance
Oxygen analyzer/controls maintenance
Air register control
Air/coal temperature control
Sootblower/air compressor maintenance
Air preheater leakage/maintenance

APPLICABILITY OF THERMAL DeNO$_x$ TO LARGE INDUSTRIAL BOILERS

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ABSTRACT

Exxon Research and Engineering Company has developed and successfully applied a process called Thermal DeNO$_x$ for removing oxides of nitrogen (NO$_x$) from flue gas in stationary combustion sources. This non-catalytic process is based on a gas phase homogeneous reaction. The technology involves injection of ammonia (NH_3) and hydrogen (H_2) into the hot flue gas within a prescribed temperature range.

Thermal DeNO$_x$ has been commercially demonstrated in gas and oil-fired steam boilers, utility boilers and process furnaces. Successful tests have also been conducted on a municipal incinerator and an oil field steam generator. Tests on flue gas generated by coal combustion have demonstrated the applicability of the process to coal-fired boilers.

Cost effectiveness of the process is superior to other competing flue gas treatment processes in most applications. Also, Thermal DeNO$_x$ is not as capital intensive as competing processes and can be applied with similar cost and performance effectiveness for either grass roots or retrofit applications.

APPLICABILITY OF THERMAL DeNO$_x$ TO LARGE INDUSTRIAL BOILERS

INTRODUCTION

Exxon Research and Engineering Company has developed and successfully applied a process (3) called Thermal DeNO$_x$ for removing oxides of nitrogen (NO$_x$) from flue gas in stationary combustion sources. This non-catalytic process is based on a gas phase homogeneous reaction (2, 5). The technology involves injection of ammonia (NH_3) into the hot flue gas within a narrow and critical temperature range. This temperature range can be significantly expanded through the additional injection of hydrogen. The NO$_x$ reduction is essentially independent of the concentration of oxides of sulfur or particulate matter in the flue gas.

Thermal DeNO$_x$ has been commercially demonstrated in gas and oil-fired steam boilers, utility boilers and process furnaces. Successful tests have also been conducted on a municipal incinerator and an oil field steam generator. Tests on flue gas generated by coal combustion have demonstrated the applicability of the process to coal-fired utility boilers, but there is no commercial experience to date. In full-scale retrofit commercial demonstrations conducted by Toa Nenryo Kogyo K.K. and Tonen Sekiyu Kagaku K.K. at their Kawasaki, Japan, plants, NO$_x$ reductions exceeding 60% were achieved (see Figure 9).

Cost effectiveness of the process is superior to other competing flue gas treatment processes in most applications. Also, Thermal DeNO$_x$ is not as capital intensive as competing processes and can be applied with similar cost and performance effectiveness for either grass roots or retrofit applications. Therefore, Thermal DeNO$_x$ offers a practical alternative in the field of NO$_x$ pollution control.

In general, Thermal $DeNO_x$ can effect reductions in NO_x emissions of up to 70% compared to the 90% reduction achievable in other processes. The specific level of $DeNO_x$ is dependent upon a number of factors, including the design or type of fired equipment, operating mode, and initial NO_x level. R&D work is continuing on this process to improve its $DeNO_x$ performance and overall process design.

Thermal $DeNO_x$ may be applied to boilers for additional NO_x reduction after combustion modifications have been made. Alternatively, in the event combustion modifications result in unacceptable losses in load capacity, Thermal $DeNO_x$ may be applied without these modifications.

PROCESS CHEMISTRY REVIEWED

The process chemistry relies on the selective reaction between NH_3 and NO_x to produce nitrogen and water. This reaction proceeds in the presence of excess oxygen within a prescribed temperature range. The overall NO_x reduction and production reactions are summarized in equations (1) and (2), respectively.

$$NO + NH_3 + O_2 + (H_2) = N_2 + H_2O \tag{1}$$

$$NH_3 + O_2 = NO + H_2O \tag{2}$$

In typical flue gas environments, the NO reduction shown as equation (1) dominates at temperatures around 1740°F (950°C). At higher temperatures, the NO production reaction shown as equation (2) becomes significant, and above 2000°F (1090°C), the injection of NH_3 is contraproductive, causing increased NO. As temperatures are reduced below 1600°F (850°C), the rate of both reactions becomes extremely low, the NO reduction falls off drastically, and the NH_3 flows through unreacted.

These very rapid changes of NO reduction with temperature are shown most clearly in Exxon's published laboratory data (4). The data shown in Figure 1 is typical of laboratory results.

Exxon's technology also includes means of altering the usable temperature range. The addition of hydrogen (H_2) extends the temperature window over a wide temperature range as shown by the laboratory data in Figure 2. At H_2/NH_3 ratios on the order of 2:1, the NO_x reduction can be forced to proceed rapidly at 1290°F (700°C). By judiciously selecting the H_2/NH_3 injection ratio, $DeNO_x$ performance can be optimized at any intermediate temperature such that the overall temperature window is as shown in Figure 3. This temperature flexibility provides load following capability on boilers and industrial heaters.

TEMPERATURE "WINDOWS" IN INDUSTRIAL BOILERS

A typical window location for industrial boilers is usually found either within the superheater tube bank or between the superheater tube bank and the steam generator tube bank. Figures 4 and 5 illustrate an injection location for a package type boiler having two symmetrical generating tube banks situated on each side of the combustion chamber. Three injectors are located interbank on each side to provide complete coverage.

The injectors for a typical field erected, cross drum design boiler are shown in Figure 6. In this boiler the injectors are located within a superheater cavity such as might be supplied for sootblowers. Support guides for the injectors are provided from attachments to the superheater tubes.

MAJOR FACTORS AFFECTING PERFORMANCE

The major factors affecting Thermal $DeNO_x$ performance are shown in Table 1. In addition to temperature and the use of NH_3 and H_2 these include:

- Residence time at temperature
- Temperature profile
- Initial NO_x
- NH_3/NO_x ratio
- Mixing

Maximizing residence time at temperature tends to enhance $DeNO_x$ performance. Typical ranges of residence time are from less than 0.1 second to greater than 1 second. In order to achieve high performance without sacrificing significant space in the boiler, residence times of 0.2 to 0.3 seconds are preferred. The most common method of providing residence time at temperature is by injecting NH_3 at the upstream side of a cavity in the tube bank as shown in Figures 4, 5, and 6.

Flue gas temperature profile at the injection plane is important in Thermal $DeNO_x$ performance since wide variations in temperature may result in a lowering of overall performance. Variations of ±100°F (56°C) can usually be accommodated without effecting performance. Larger variations may require hydrogen injection in the lower temperature zone(s) of the injection plane in order to maintain acceptable performance.

In order to accommodate temperature changes in the post-combustion zone of a boiler resulting from changes in boiler load, more than one ammonia injection grid may be required in order to maintain satisfactory $DeNO_x$ performance. For example, as load is reduced from full to 50%, the temperature for optimum Thermal $DeNO_x$ will shift toward the fire box. Temperature shifts can also occur in coal fired boilers due to slagging, type of coal, changes in excess O_2 and other operational variations. In addition, the use of hydrogen with its ability to widen the effective $DeNO_x$ temperature window increases the capability to deal with a wide range of boiler operating conditions. Selection of grid locations can be accomplished by temperature measurement in the case of existing boilers or in conjunction with boiler vendor performance predictions in the case of grass roots designs.

The process is also sensitive to initial NO_x and NH_3 concentrations. The NH_3 injection rate is generally expressed as a mole ratio relative to the initial NO_x concentration. NH_3/NO_x ratios of 1.5 are common for initial NO_x levels of 200 vppm and less. As initial NO_x concentration increases, the ratio is reduced toward 1.0. Ammonia breakthrough levels are generally below 50 vppm.

NEW MIXING TECHNOLOGY BOOSTS PERFORMANCE

Recent innovations in mixing techniques have led to substantially increased performance capability with the Thermal $DeNO_x$ process. This is especially true in short residence time situations normally encountered in utility and industrial boiler applications.

For comparison purposes, three NH_3 injection/mixing techniques are shown on Figure 7. You will note that substantial improvements in performance have been achieved through development of an improved NH_3 injection technique. These data have been taken in our 30 MBtu/hr (8.8 MW) pilot plant test furnace.

In addition, pilot plant testing has shown that staged injection of hydrogen utilizing two grids in succession results in further increases in performance. These technological advances will result in performance predictions in the range of 70% or more for grass roots utility boiler applications and 60% to 70% for retrofit applications.

The impact of these advances in technology are illustrated in Figure 8. This figure shows performance predictions for a retrofit utility boiler application for three different conditions:

- single grid, no H_2
- single grid, zoned H_2
- two grids with staged H_2

A maximum performance improvement at 100% load of 24 $DeNO_x$ percentage points (from 41% to 65%) is possible here through utilization of the new technology.

PROVEN PERFORMANCE

Thermal $DeNO_x$ has been successfully demonstrated in gas and oil-fired utility boilers, package and field erected industrial boilers, process furnaces and oil field steamers as summarized in Table 2. Actual performance often represents a compromise between the technical limits of the process chemistry and cost effectiveness. In many situations, performance is maximized at full load operation, and smaller NO_x reductions accepted at reduced loads with the lower reaction zone temperatures. In such installations, total NO_x emissions are generally at target levels over the full spectrum of operating conditions because of the reduced NO_x production rate at lower loads. Results from seven demonstrations are shown over their range of operating conditions as a function of flue gas temperature in Figure 9. Please note that these units incorporate earlier mixing technology and thus performance shown is generally lower than would be achieved with updated technology.

Alternative designs are available to suit the load demands of the particular boiler or furnace. Of the units installed to date, some have been designed for base load operation, while others accommodate all operating conditions from 50-100% of design capacity. As another example, one boiler in which Thermal $DeNO_x$ was installed operates between 35 and 50% of design, and the process was designed for these load conditions.

Applicability and effectiveness will vary from one unit to the next depending on local flue gas conditions and on the configuration of the high temperature zones. Preliminary estimates of performance expected to be achieved for retrofitting Thermal $DeNO_x$ into existing units can be made on the basis of engineering drawings and design specifications. Exxon can also provide recommendations for designing new boilers and furnaces and for modifying existing designs so as to maximize the efficiency of the process.

Most of the development of the Thermal $DeNO_x$ process has taken place on oil-fired sources, essentially free of fly ash. Fly ash from coal firing may deposit on injector grids, change gas flow patterns and temperature profiles and foul or erode injection nozzles. The extent to which reliable performance can be provided under these conditions remains to be proven. We do not feel significant or insuperable problems will arise. However, we would propose a demonstration test be performed to evaluate these factors on an existing boiler. Details of this demonstration test can be provided upon request.

WHAT ABOUT REACTIONS WITH SULFUR?

Detailed laboratory experiments have shown there are no reactions between the Thermal $DeNO_x$ process and sulfur compounds in the high temperature flue gas regions. That is, sulfur or its oxides do not interfere with the NH_3-NO_x-O_2-H_2 chemistry. Additionally, ammonia injection has been shown to cause neither additional homogenous nor additional heterogeneous oxidation of SO_2 to SO_3.

To the extent that the thermal reduction of NO_x leaves some NH_3 unreacted, and as the combustion gases cool, NH_3 reacts with SO_3 and H_2O to form ammonium sulfate ($(NH_4)_2SO_4$) and/or ammonium bisulfate (NH_4HSO_4). Ammonium sulfate is a dry solid which forms directly from the gaseous reactants without passing through the liquid state. It is not corrosive or appreciably hygroscopic. When the sulfate is formed in flue gas the resulting particles are on the order of 1-3 microns. Thus the sulfate should pass through the air preheater with very little deposition. When heated, ammonium sulfate decomposes to ammonium bisulfate and gaseous ammonia.

Ammonium bisulfate is a sticky liquid at air preheater temperatures. The melting point of pure ammonium bisulfate is 297°F (147°C), which is below the temperature of the flue gas leaving most air preheaters, but is above the metal temperature. However, the presence of H_2SO_4 or small amounts of ammonium sulfate depress the melting point to about 266°F (130°C). So ammonium bisulfate deposits should be liquid throughout most of the air preheater, with solid deposits only at the extreme cold end. The sticky liquid is corrosive and tends to trap ash and soot particles, accelerating the rate of deposit build-up.

Ammonium bisulfate formation can be minimized by either of three principal means:

- Limiting NH_3 breakthrough to 5 vppm or less.
- Maintaining flue gas temperature at the preheater outlet above 400°F (204°C).
- Maintaining an $NH_3:SO_3$ molar ratio above 2.0 and providing sufficient residence time for the reactants to form ammonium sulfate rather than bisulfate.

In most cases the last method is the most practical for application with the Thermal $DeNO_x$ process, since typical NH_3 breakthrough levels (approximately 50 vppm) are usually twice that of SO_3. Also, maintaining a high flue gas outlet temperature is impractical since this represents a 2-3% loss in thermal efficiency for many boilers. A summary of the fouling/corrosion potential of ammonium sulfates as a function of NH_3 and SO_3 concentrations in flue gas is presented in Figure 10.

Based on laboratory and commercial tests with oil firing, these sulfates when in combination in ash deposits do not create either severe corrosion or unacceptable air preheater fouling problems when Thermal $DeNO_x$ is used in accordance with its design specifications. However, we would expect both fouling and corrosion to increase if bisulfate formation is not curtailed. In addition, long term tests conducted in two oil-fired boilers by Tonen Sekiyu Kagaku K.K. in Kawasaki, Japan, revealed sulfate/bisulfate deposits could easily be removed by waterwashing the air preheaters at reasonable intervals.

ENGINEERING CONSIDERATIONS

Although the chemistry is straightforward, certain difficulties must be overcome when applying the process to commercial equipment. Performance is generally limited by the access to the required flue gas temperature range of the reaction, and the dependence of the reaction on the local concentrations of reactants, NH_3, NO_x, O_2, and H_2. Exxon's technology provides a means of adapting the chemistry requirements to industrial equipment environments, and significant NO_x reductions can be achieved by the use of Thermal $DeNO_x$ technology in existing boilers. Application to new, grass-roots designs is usually easier because the internal configuration of the cavity at the required temperature can be readily adjusted to complement the process demands.

Accommodating flue gas temperature variations is important if high $DeNO_x$ rates are to be achieved. Not only does the system have to accommodate flue gas temperature changes caused by normal load and operating variations, but it also must allow for fluctuations across the reaction zone caused by non-uniformities in flow and heat transfer. It follows, therefore, that a case-by-case evaluation of flue gas temperatures and local conditions is required for the application of Thermal $DeNO_x$ for each installation considered.

Initially, ammonia was injected only into boiler cavities, boiler regions between tube banks, which can be considered to be isothermal to a first approximation. Subsequent experimentation by Exxon Research has shown the feasibility of injecting ammonia into boiler tube bank regions as well. Thus, satisfactory NO reduction performance can be obtained by locating the injector grid in either the boiler convection pass cavities or tube bank. The ability to inject ammonia at virtually any post-combustion boiler location where temperatures range from 1292 to 1994°F (700 to 1090°C) has substantially increased the flexibility of the Exxon Thermal $DeNO_x$ Process.

SUPERIOR COST EFFECTIVENESS

The Thermal $DeNO_x$ process offers one of the most practical approaches to significant NO_x reduction from stationary fired equipment of any post-combustion NO_x removal process currently on the market. This is due to the fact that the process is far less capital intensive and achieves superior cost effectiveness even though NO_x reduction levels are somewhat lower than other processes.

In order to demonstrate cost effectiveness of the process, a 200,000 lb/hr (91 t/hr) industrial boiler has been chosen for illustration purposes. A Thermal $DeNO_x$ equipment sizing basis is presented in Table 3 and a simplified flow diagram is shown on Figure 11. It is assumed that the boiler is oil or gas fired and has an uncontrolled NO_x level of 200 vppm corrected to 3% O_2 dry. The boiler is to be equipped with a single grid capable of injecting both NH_3 and H_2 via a steam carrier. A one month NH_3 storage capacity has been provided, and H_2 is supplied through an ammonia dissociator.

The total erected capital investment for these facilities is estimated to be $472,000 as outlined in Table 4. Direct costs include the material and labor for equipment outlined in Table 3 plus interconnecting piping. Indirect costs include field labor overheads, construction superivision and equipment, labor wage taxes, erection fee, engineering costs, and licensing fee. Contingency is based on 30% of direct, plus indirect cost less licensing fee. Costs are expressed at 1Q81 southern California level. Excluded from these costs are such items as land and owners charges.

Cost effectiveness for the sample boiler installation is also shown in Table 4 for three different bases. Annualized costs are obtained by assuming a five year payout on investment plus annual operating costs. On a heat fired basis, cost effectiveness of the process is $0.13 per M Btu (.04 mill/kWh). The cost effectiveness based on NO_x removed is $1.51 k/US ton NO_2 ($1.66 k/t NO_2) for a $DeNO_x$ efficiency of 60% and $1.29 k/US ton NO_2 ($1.42 k/t NO_2) for 70% $DeNO_x$. This cost compares favorably with some combustion modification techniques such as burners out of service and flue gas recirculation, and is substantially lower than selective catalytic reduction.

Annual operating costs are shown in Table 5. These costs are based on a 65% annual load factor and include values for NH_3, power and steam consumption and maintenance material and labor.

SUMMARY

In summary, Thermal $DeNO_x$ represents one of the most practical and cost effective means of flue gas treatment for NO_x control currently available in the market place. As the requirement for control of NO_x emissions becomes more stringent and more widespread, application of NO_x control technology will become necessary in many areas of the U.S.A. Recent technological advances have resulted in significant increases in Thermal $DeNO_x$ performance with negligible increase in investment thus further improving its cost effectiveness. No technological difficulties are foreseen in applying Thermal DeNO$_x$ to all types of industrial boilers including coal fired, but a test in a coal fired boiler is needed to demonstrate the applicability of the technology and optimize engineering design considerations.

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14. Bartok, W., and G. M. Varga, "Applicability of the Thermal $DeNO_x$ Process to Coal-Fired Utility Boilers," American Flame Research Committee International Symposium on NO_x Reduction in Industrial Boilers, Heaters and Furnaces, Houston, October, 1979.

FIGURE 1

TEMPERATURE "WINDOW" FOR THERMAL DENOx REACTION-NH3 ONLY

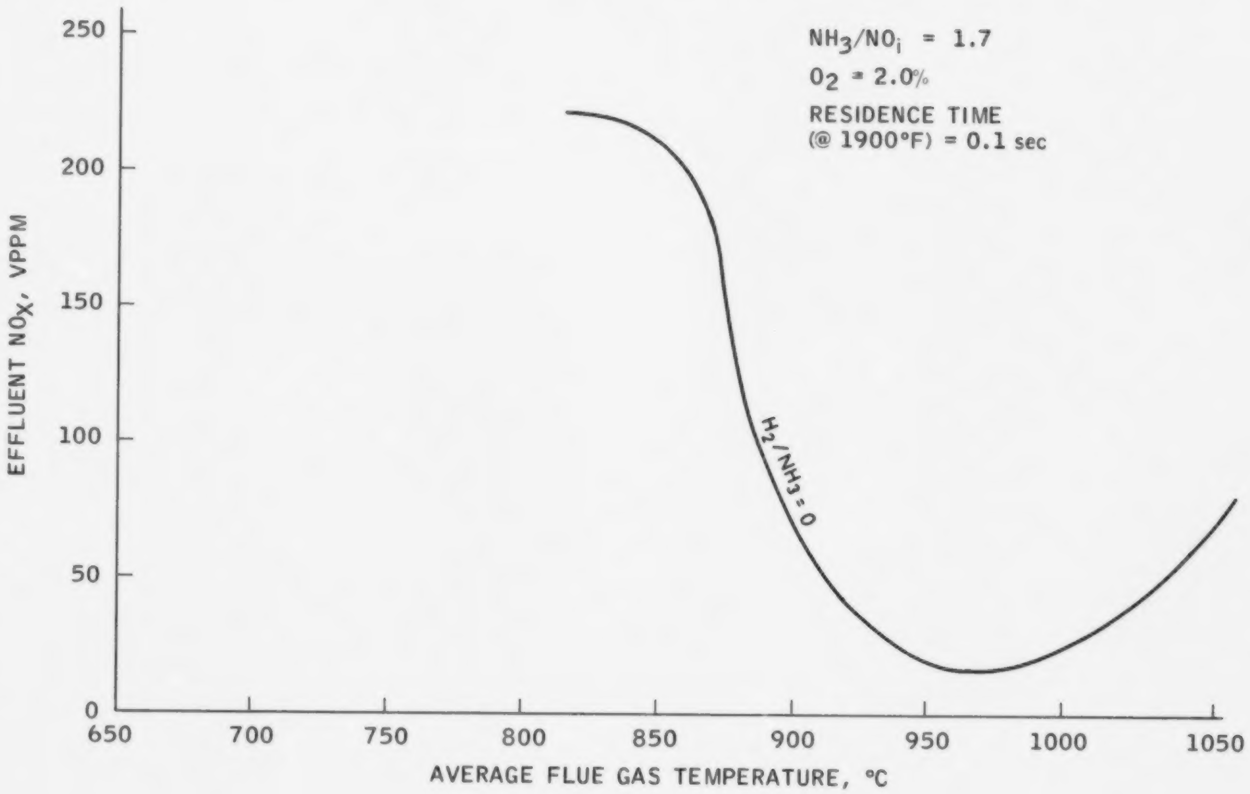

FIGURE 2

TEMPERATURE "WINDOW" FOR THERMAL DENOx REACTION-H_2+NH_3

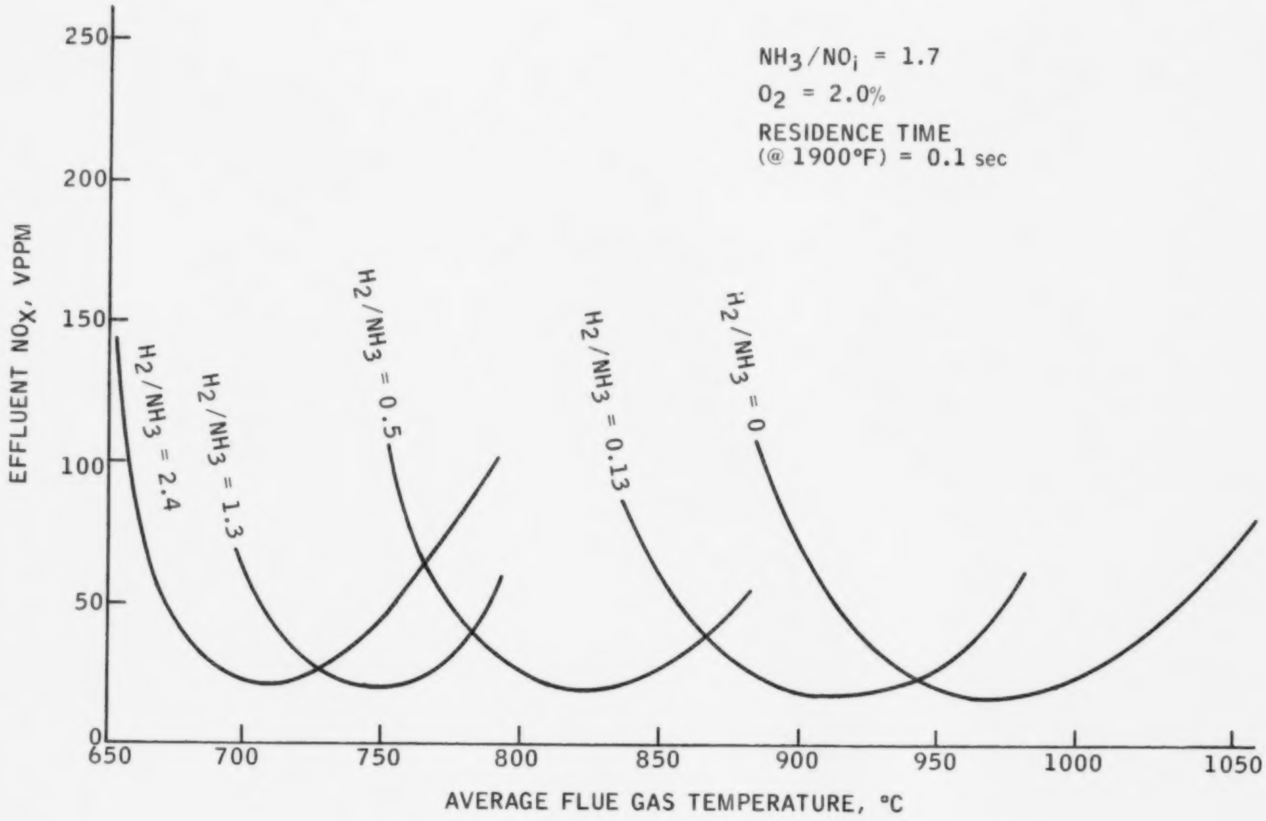

FIGURE 3

TEMPERATURE “WINDOW” FOR THERMAL DENOx REACTION

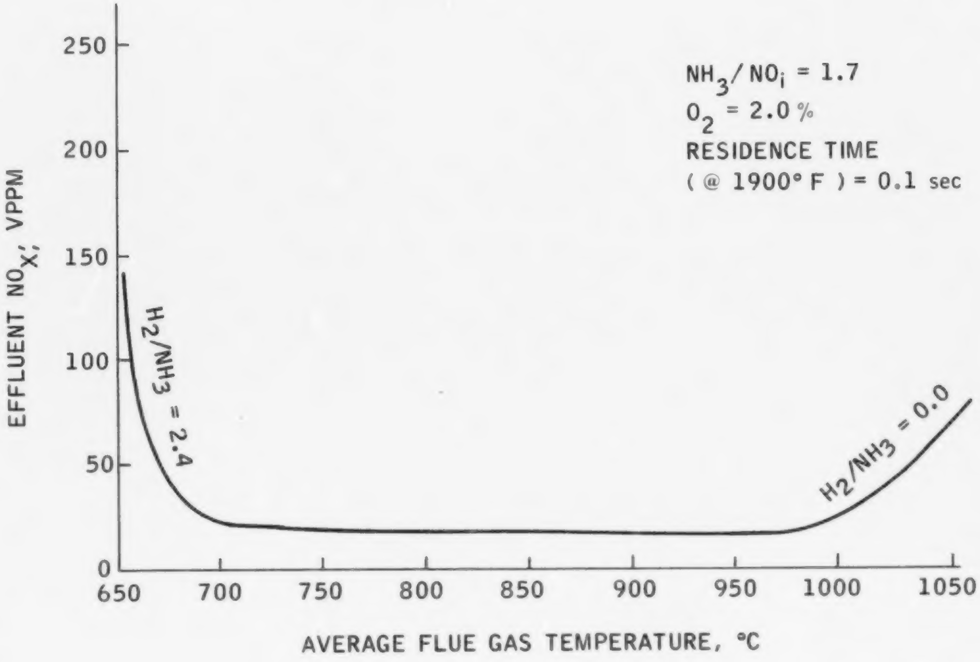

FIGURE 4

TYPICAL PACKAGE BOILER THERMAL DENOx INJECTOR DESIGN
(Rear View)

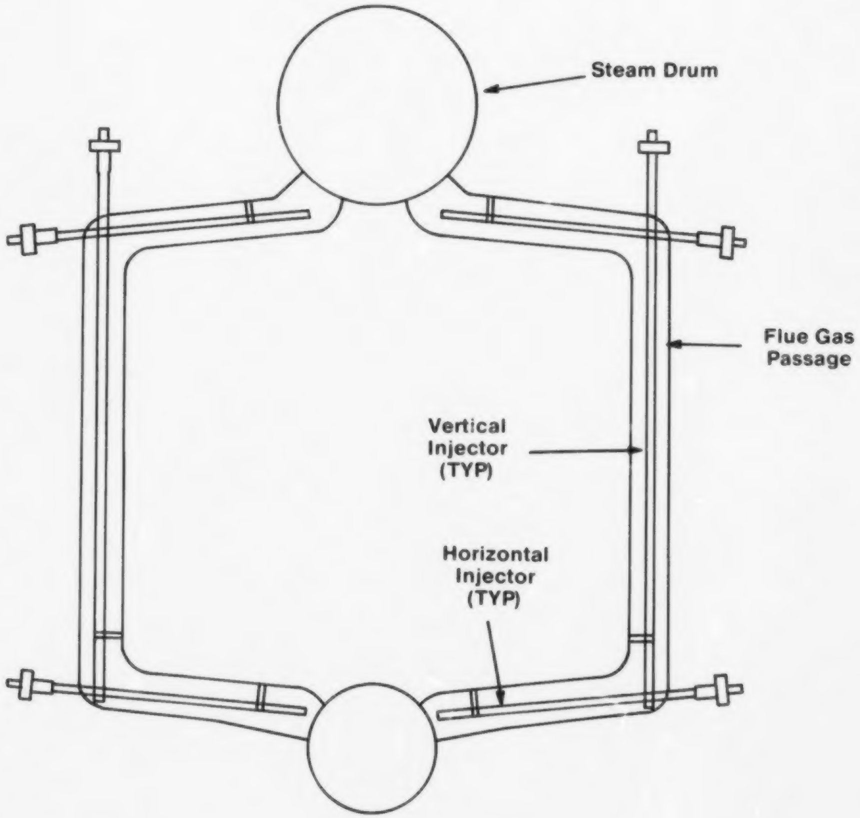
Steam Drum
Flue Gas Passage
Vertical Injector (TYP)
Horizontal Injector (TYP)

FIGURE 5

TYPICAL PACKAGE BOILER THERMAL DENOx INJECTOR DESIGN
(Plan View)

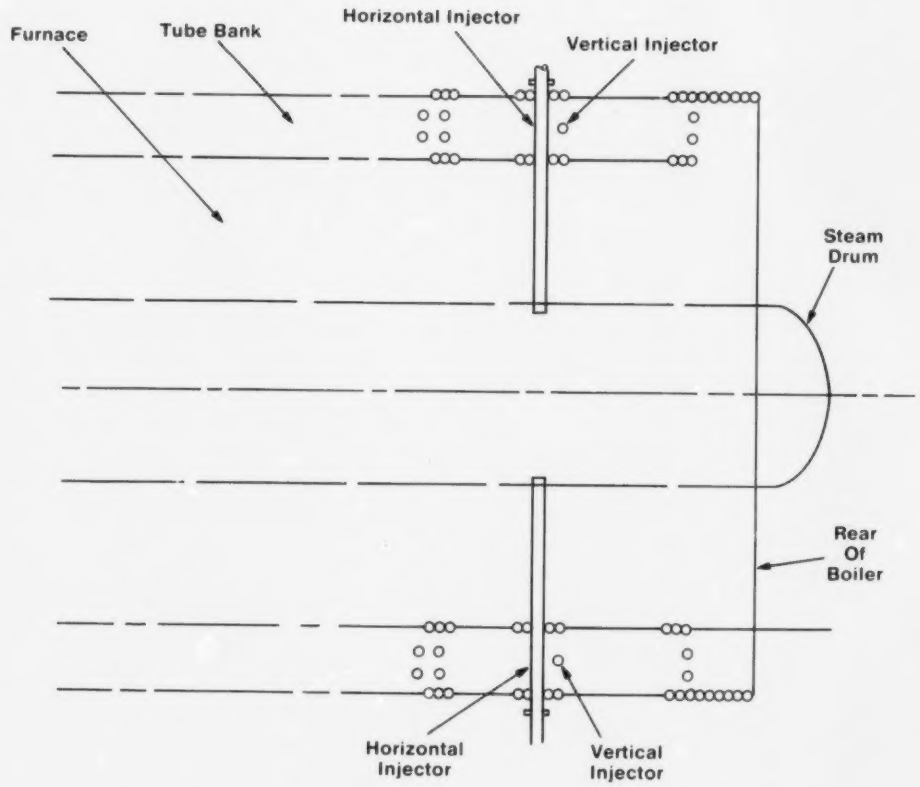
Furnace
Tube Bank
Horizontal Injector
Vertical Injector
Steam Drum
Rear Of Boiler
Horizontal Injector
Vertical Injector

FIGURE 6

TYPICAL CROSS DRUM BOILER THERMAL DENOx INJECTOR DESIGN

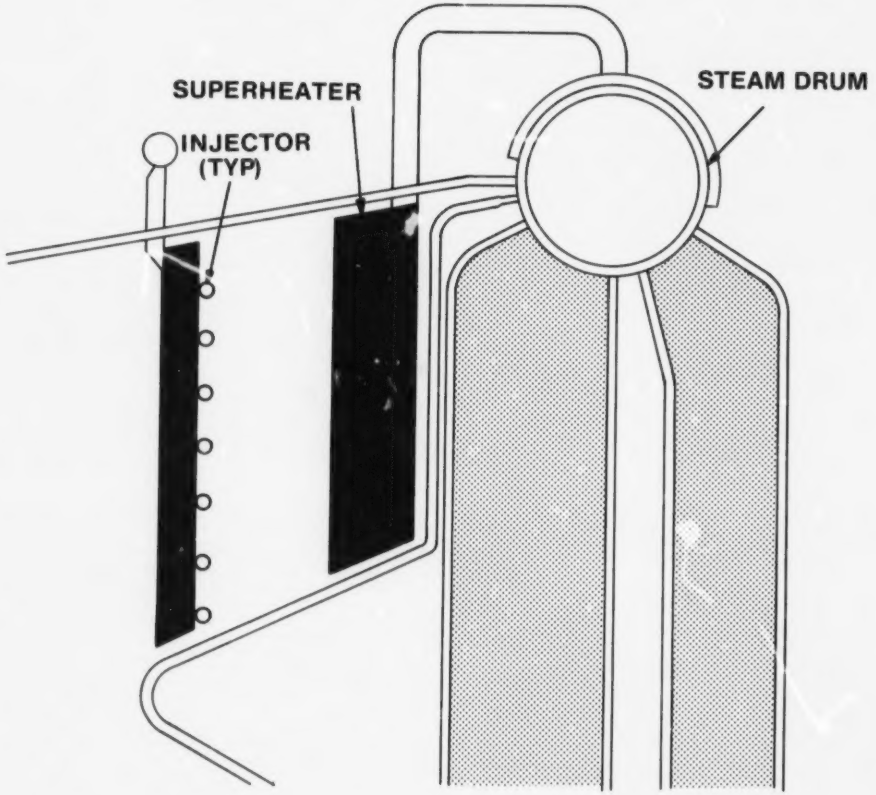
SUPERHEATER
INJECTOR (TYP)
STEAM DRUM

FIGURE 7

DENOx PERFORMANCE IN PILOT PLANT TESTS USING VARIOUS MIXING TECHNIQUES

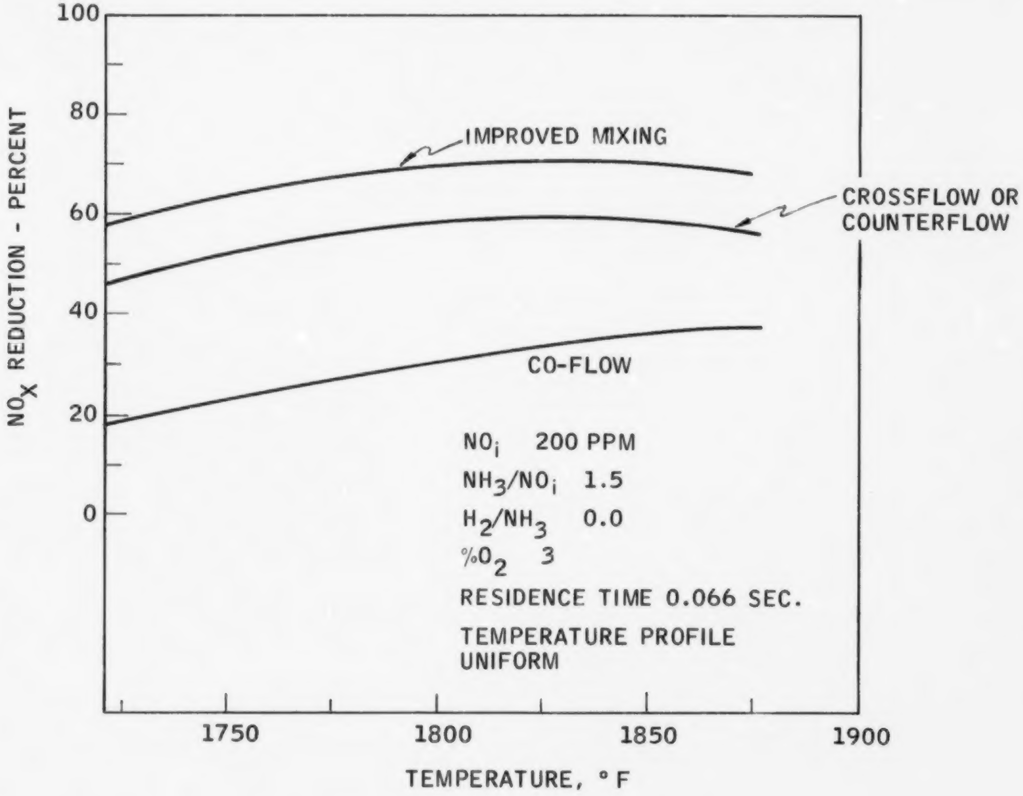

FIGURE 8

UTILITY BOILER PERFORMANCE PREDICTIONS EFFECTS OF IMPROVED MIXING AND HYDROGEN ADDITION

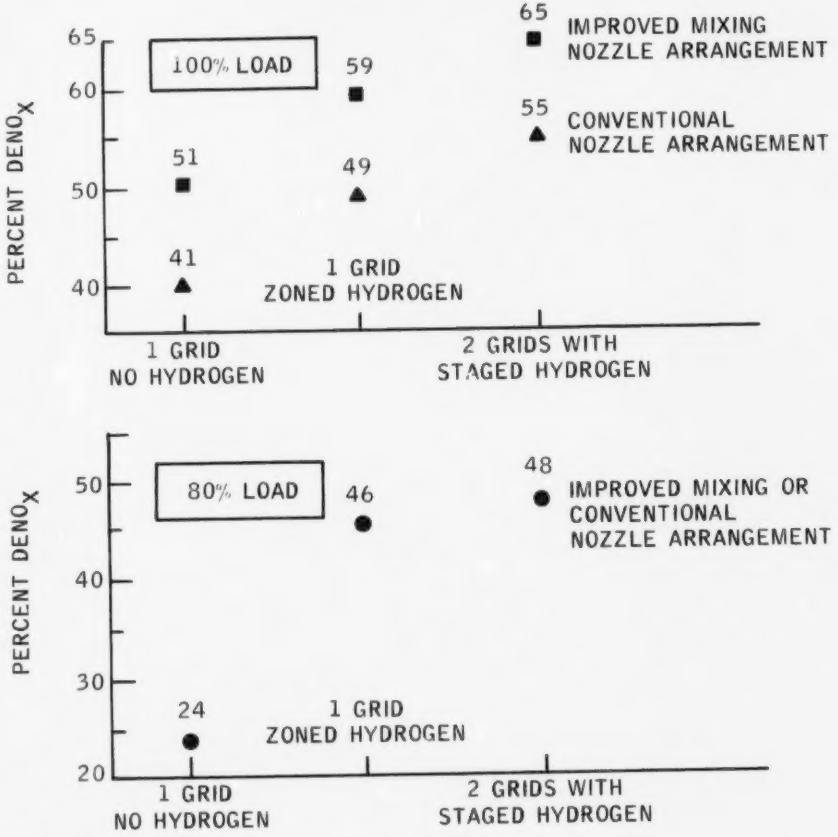

FIGURE 9

PERFORMANCE OF THERMAL DENOx SYSTEMS IN COMMERCIAL APPLICATIONS

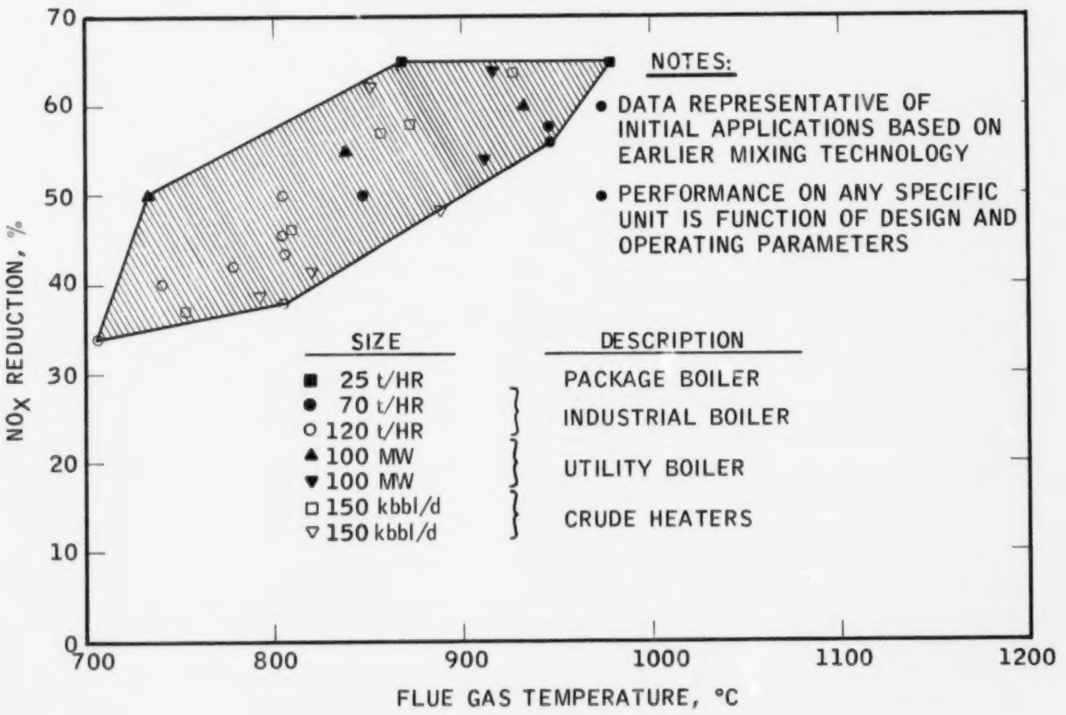

FIGURE 10

FOULING POTENTIAL OF AMMONIUM SULFATES

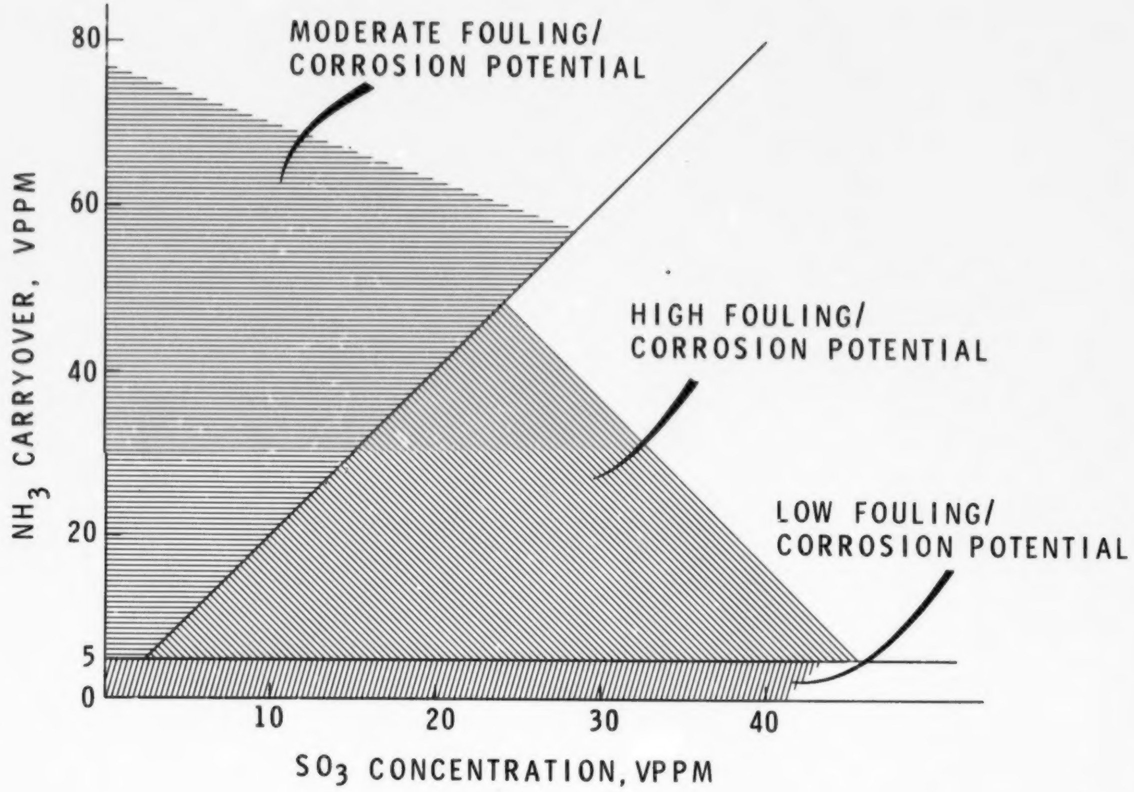

FIGURE 11

SIMPLIFIED THERMAL DENOx SUPPLY SYSTEM FLOW DIAGRAM

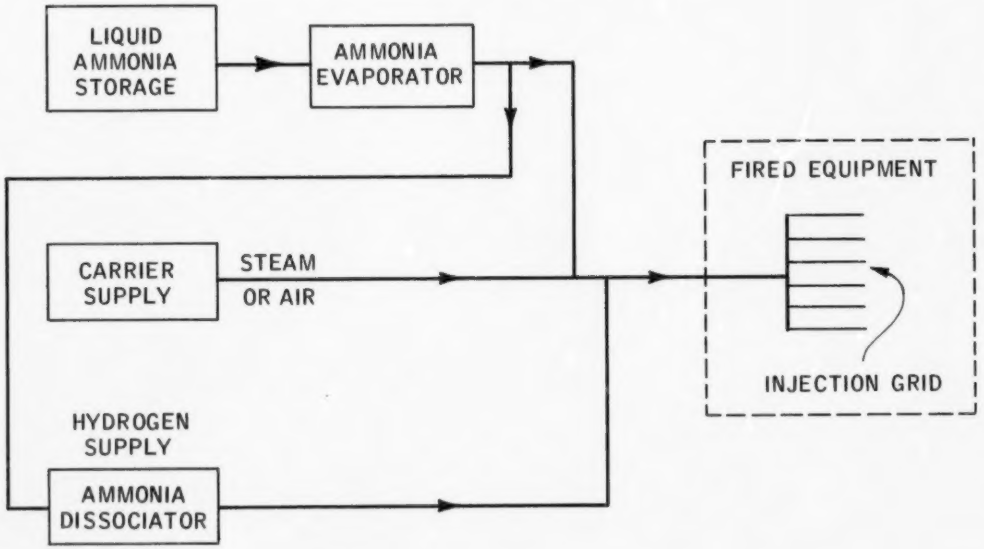
LIQUID AMMONIA STORAGE
AMMONIA EVAPORATOR
CARRIER SUPPLY
STEAM OR AIR
HYDROGEN SUPPLY
AMMONIA DISSOCIATOR
FIRED EQUIPMENT
INJECTION GRID

TABLE I

MAJOR FACTORS IN THERMAL DENOx PERFORMANCE

- FLUE GAS TEMPERATURE -
  - + WITH OR WITHOUT H_2
- RESIDENCE TIME AT TEMPERATURE
- TEMPERATURE PROFILE
- INITIAL NO_x
- NH_3/NO_x RATIO
- MIXING

TABLE II

THERMAL DENOx EXPERIENCE SUMMARY (OIL AND GAS FIRED UNITS)

	OPERATIONAL	CONSTRUCTION PHASE	DESIGN PHASE
JAPANESE INDUSTRIAL BOILERS	3		
JAPANESE UTILITY BOILERS	5		
JAPANESE PETROLEUM HEATERS	4		
CALIFORNIA OIL FIELD STEAMER (DEMONSTRATION)	1		
CALIFORNIA FLAT GLASS MELTING FURNACE (DEMONSTRATION)	1		
CALIFORNIA PETROLEUM HEATERS	2	19	5
CALIFORNIA UTILITY BOILER		1	
CALIFORNIA INDUSTRIAL BOILERS		3	
CALIFORNIA INCINERATORS			2

TABLE III

EQUIPMENT SIZING BASIS FOR PERMANENT THERMAL DENOx FACILITIES FOR SAMPLE INDUSTRIAL BOILER

BOILER DESIGN CONDITIONS	200,000 LB/HR, 615 PSIG, 700 F
FUEL	OIL OR GAS
INITIAL NO_X	200 PPM
NH_3/NO_X	1.5
H_2/NH_3	0.5
CARRIER REQUIREMENT	STEAM, 1500 LB/HR, 15 PSIG (MINIMUM)
NH_3 STORAGE TANK	30 DAY STORAGE CAPACITY (8000 GALLONS)
NH_3 VAPORIZER	(1) ELECTRIC ELEMENT, DIRECT CONTACT
NH_3 DISSOCIATOR	(1) 750 SCFH
INJECTION GRID	SINGLE LOCATION
INSTRUMENTATION	AS REQUIRED

TABLE IV

THERMAL DENOx INVESTMENT COST AND COST EFFECTIVENESS FOR SAMPLE INDUSTRIAL BOILER

CAPITAL INVESTMENT(1)	
MATERIAL AND LABOR(2)	\$168 K
INDIRECT COSTS(3)	\$215 K
CONTINGENCY(4)	\$ 89 K
	\$472 K
COST EFFECTIVENESS	
\$/M BTU FIRED	0.13
K\$/TON NO_x REMOVED @ 60% $DeNO_x$	1.51
K\$/TON NO_x REMOVED @ 70% $DeNO_x$	1.29

NOTES: (1) INVESTMENT COSTS ARE EXPRESSED AT IQ81 SOUTHERN CALIFORNIA LEVEL

(2) INCLUDES EQUIPMENT ITEMS LISTED IN TABLE III PLUS INTERCONNECTING PIPING

(3) INCLUDES FIELD LABOR OVERHEADS, CONSTRUCTION SUPERVISION AND EQUIPMENT, LABOR WAGE TAXES, ERECTION FEE, CONTRACTOR ENGINEERING, EXXON RESEARCH AND ENGINEERING CO. CHARGES, AND LICENSING FEE. EXCLUDED ARE SUCH ITEMS AS LAND AND OWNERS CHARGES.

(4) CONTINGENCY IS BASED ON 30% OF DIRECT COSTS PLUS INDIRECT COSTS MINUS LICENSING FEE.

TABLE V

THERMAL DENOx ANNUAL OPERATING COST FOR SAMPLE INDUSTRIAL BOILER

ITEM	ANNUAL CONSUMPTION(1)	UNIT GAS	ANNUAL COST
AMMONIA(2)	165 TONS	$170/TON	$27,965
ELECTRIC POWER(3)	136 MWH	$50/MWH	6,800
STEAM(4)	4290 TONS	$12/TON	51,480
MAINTENANCE MATERIAL AND LABOR(5)			11,760
		TOTAL	$98,005

NOTES:

(1) ASSUMES 65% LOAD FACTOR

(2) INCLUDES AMMONIA FOR DIRECT INJECTION PLUS HYDROGEN PRODUCTION

(3) INCLUDES POWER REQUIREMENT FOR AMMONIA VAPORIZER AND DISSOCIATOR

(4) LOW PRESSURE STEAM (15 PSIG MINIMUM) FOR CARRIER

(5) ASSUMED TO BE 7% OF DIRECT INVESTMENT COST

CONVENTIONAL COMBUSTION ENVIRONMENTAL ASSESSMENT PROGRAM

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ABSTRACT

The Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina, has developed and implemented a major program for the assessment of the environmental, economic, and energy impacts of multimedia pollutant emissions from stationary residential, commercial, institutional, industrial, and utility combustion processes. The Conventional Combustion Environmental Assessment (CCEA) Program has become a major source of data and information for Agency use in developing and modifying standards and control technologies.

This paper presents the theme, objectives, pollutants of concern, current activities, and some representative data from CCEA Program projects. Included are data from: 1) a comparative assessment of coal and oil firing in an industrial boiler, 2) environmental assessments of an 820 MW, FGD-controlled, coal-fired utility boiler and a 342 MW oil-fired utility boiler, 3) a 170-site field study of combustion sources, 4) dry bottom industrial boilers firing pulverized coal, 5) residential coal combustion, and 6) wood combustion studies.

1. INTRODUCTION

EPA's Industrial Environmental Research Laboratory at Research Triangle Park, NC, initiated the Conventional Combustion Environmental Assessment (CCEA) Program in February 1977. The primary purpose of the CCEA Program is to assess the environmental, economic, and energy impacts of stationary conventional processes firing coal, oil, wood, derived fuels, waste materials, and combinations of these fuels. The assessment results achieved in the CCEA Program are used in the Agency to ensure that the environmental impacts of the expanded use of conventional combustion processes for energy production are kept within acceptable limits. This paper presents the theme, objectives, pollutants of concern, current activities, and some representative data from the CCEA Program.

2. CCEA PROGRAM THEME AND OBJECTIVES

The central theme and focus of the CCEA Program is the assessment of hazardous pollutants in the gaseous emission streams from conventional combustion processes. The Program is also concerned with those pollutants which degrade water and land quality after removal from air emission streams (cross media impacts). In keeping with the CCEA Program theme, three specific objectives have been established for the Program:

a. Assess the controllability of hazardous pollutants, including costs, removal efficiencies, schedules (for emerging technologies), and energy penalties.

b. Assess the environmental impacts of hazardous pollutants from conventional combustion processes operating at baseline, transient, and modified conditions (pollutants emitted, quantities emitted, biological characterization, and impact projections).

c. Identify need for risk assessments and provide supporting information for risk assessments which may be conducted subsequently by other Agency offices.

3. POLLUTANTS

In meeting the three objectives specified above, the CCEA Program is considering some top priority pollutants including hazardous or toxic organic compounds and hazardous or toxic metals. For example, the CCEA Program studies have determined that the emission levels of polycyclic organic matter (POM) from wood combustion are high enough to cause concern for potential environmental impacts and to warrant the commitment of additional resources to better define the magnitude of the problem and to investigate techniques for mitigating the impacts. In addition to the assessment of the impacts of wood combustion during 1981 and 1982, the Program will also continue to characterize and assess the emissions of the top priority pollutants which result from the combustion of other fuels, including coal, oil, derived fuels, waste solvents, and combinations of these fuels.

4. SUMMARY OF CURRENT MAJOR PROGRAM ACTIVITIES

The CCEA Program is a comprehensive, coordinated effort to assess the environmental impacts of conventional combustion processes and associated pollution control technologies. The Program is comprised of several projects each of which makes a contribution to the overall goals and objectives of the Program. In the interest of brevity, this section will provide an overview of some of the major projects.

Emissions Assessment of Conventional Combustion Systems (EACCS) - The EACCS project is a major contributor to the CCEA Program data base. The EACCS project, a 4-year effort which will end in September 1980, collected field data on multimedia emissions from 51 classes of conventional stationary combustion sources. Prior to initiating field testing, existing data from each class of combustion sources were assembled and evaluated to determine areas in which data were scarce, of questionable accuracy, or non-existent. Based on the results of this evaluation of existing data, field testing of 171 combustion sources was scheduled and conducted.

These field tests have filled data gaps, augmented existing data, and produced some important findings. For example, the study of stationary internal combustion sources verified the significant contribution that these sources make to the national emissions of NO_x and hydrocarbons. In addition, oil-fired residential furnaces were found to be significant sources of NO_x, SO_3, and Ni. Initial data indicate that POM emissions from residential and industrial wood combustion may be alarmingly high, and extensive investigation of POM emissions from wood combustion is being planned as a result.

Selected data from the EACCS project are presented in Section 5 of this paper. The current status of the EACCS reports on various combustion source categories surveyed is presented below:

1) Reports Published:

- Methods and Procedures Manual for Sampling and Analysis
  EPA-600/7-79-029a (NTIS PB 294675)

- Gas- and Oil-Fired Residential Heating Sources
  EPA-600/7-79-029b (NTIS PB 298494)

- Internal Combustion Sources
  EPA-600/7-79-029c (NTIS PB 296390)

- Environmental Assessment of a Coal-Fired Controlled
  Utility Boiler (LaCygne Station, Kansas City Power
  and Light Company)
  EPA-600/7-80-086 (NTIS PB 80-187735)

- Environmental Assessment of an Oil-Fired Controlled
  Utility Boiler (Haynes Station, Los Angeles Department
  of Water and Power)
  EPA-600/7-80-087 (NTIS PB 80-190085)

2) Reports Currently in Draft Form:

- Commercial/Institutional Source Category
- Utility (External Combustion) Source Category

3) Reports Scheduled for Completion in 1980:

- Environmental Assessment of NIPSCO's Mitchell Station (Wellman-Lord FGD System)
- Environmental Assessment of Louisville Gas and Electric's Cane Run Station (Dual Alkali FGD System)
- Industrial Source Category
- EACCS Final Summary Report

Environmental Assessment of Stationary Source NO_x Control Technologies - Like EACCS, this project is also a major contributor to the CCEA Program data base. The overall objectives of this project are to (1) assess the environmental impacts of stationary combustion sources and NO_x controls and (2) identify cost-effective, environmentally sound NO_x control technologies that can be used to meet NO_2 emission and air quality standards. The project - initiated in June 1976 and concluded in November 1979 - filled data gaps, augmented the CCEA data base, and produced significant and useful findings. For example, the study showed that coal firing produces the greatest discharge severity (see Glossary) and that the flue gas stream dominates environmental impacts. Among flue gas components, NO_x and SO_2 generally account for more than 50 percent of the discharge severity associated with the entire flue gas stream. In addition, the preliminary study results suggest that no definitive trend exists between POM emissions and low NO_x operation. Selected data from this project are presented in Section 5 of this paper. The current status of the NO_x EA reports is presented below:

1) Reports Published:

   - Preliminary Environmental Assessment of Combustion Modification Techniques (EPA-600/7-77-119a and b; NTIS PB 276680 and 276681)

   - SAM/IA: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents (EPA-600/7-78-015; NTIS PB 276088)

   - Environmental Assessment of Stationary Source NO_x Control Technologies: First Annual Report (EPA-600/7-78-046; NTIS PB 279083)

   - Emission Characterization of Stationary NO_x Sources (EPA-600/7-78-120a and b; NTIS PB 284520 and 285429)

   - Environmental Assessment of Stationary Source NO_x Control Technologies: Second Annual Report (EPA-600/7-79-147; NTIS PB 300469)

2) Reports Currently in Draft Form:

   - Internal Combustion Engine Special Report

   - Environmental Assessment of Stationary Source NO_x Control Technologies: Final Report

Combustion Modification Environmental Assessment - The main objective of this project is to continue the environmental assessment of combustion control technology initiated under the project above. This project will produce environmental assessment test programs including individual source test reports and special reports. The test programs will determine the effects of combustion modifications through chemical analysis, bioassay testing, and operating data evaluation. Initiated in December 1979, this project will assess 10 sites per year over the next 3 years.

1) Reports Published: None

2) Reports Currently in Draft Form: None

3) Reports Scheduled for Completion in 1980:

   - Individual Site Reports and Data Supplement Reports for Sites 1-10 (9/80 - 12/80)
   - Special Report 7/80
   - Special Report 11/80

Environmental Assessment of Wood Combustion - Preliminary data from CCEA projects and from the work of other researchers have indicated that the quantities of POM emitted from residential, commercial, and industrial wood combustion are significant in comparison to quantities emitted when other fuels are burned. Data in this area are scarce, and there is a pressing need to better delineate the nature and magnitude of the problem. As a result, the CCEA Program has undertaken the development of a comprehensive wood combustion research and development program which began in FY 79 and will be greatly expanded in FY 81. The wood program will include the characterization and environmental assessment of emissions from various residential, commercial, and industrial wood combustors.

The program will also include ambient sampling to determine POM concentrations in a community in which wood is the predominant fuel. In addition, the basic process of wood combustion under various conditions will be evaluated along with combustor types and operating techniques to determine feasible approaches for minimizing potentially harmful emissions from wood combustion processes. This comprehensive program will be initiated in December 1980.

5. REPRESENTATIVE DATA

The CCEA Program has compiled an extensive environmental assessment data base dealing with a broad range of conventional combustion equipment and a variety of fuels and fuel combinations. CCEA field data and the assessment and evaluation of these and other data have produced significant results and findings that identify and elucidate environmental problems that are of concern to the Agency and to industry as well. The data below are presented as examples of representative data, findings, and conclusions that are being developed in the CCEA Program.

EACCS Project - Environmental Assessment of Coal Vs. Oil Firing - A comprehensive enviromental assessment of a 10 MW industrial boiler has been completed under the direction and sponsorship of the CCEA Program. The final report (EPA-600/7-78-164a, b, and c; NTIS PB 289942, 289941, and 291236) describes the results of sampling and analysis in a dual fuel process steam boiler operated by Firestone Tire and Rubber Company. The boiler, equipped with an FMC dual alkali FGD pilot scrubber, was originally designed to burn coal and later modified to burn either high volatile eastern bituminous coal or No. 6 fuel oil.

The difference in environmental impacts between coal and oil combustion emissions from industrial boilers controlled only by FGD is potentially significant. Even so, the report concludes that other factors may override fuel choice in determining the environmental acceptability of controlled industrial boilers. Such factors include location, type, and number of other emission sources; background pollution levels; and the potential long-term accumulation of pollutants to unacceptable levels in the environment.

The dual alkali scrubber operated at SO_2 and particle removal efficiencies of 96 and 99 percent, respectively. At these conditions, emissions of NO_x, CO, and organics (as CH_4) from coal firing were about three times as great as those from oil firing. But the ratio of coal to oil emissions for SO_2, SO_3, sulfate, and total particles was in the range of 0.8 to 1.5. Models applied to this specific location and plant indicate that estimated ambient NO_x concentration produced by coal firing (double those produced by oil firing) would exceed the National Ambient Air Quality Standards (NAAQS) for NO_x without controls.

Coal firing produced higher trace element concentrations in the scrubber cake than oil firing, but quantities of heavy metals and toxic substances in the scrubber cake from both fuels would require disposal controls to prevent leaching and ground water contamination.

Emissions of cadmium from oil firing and molybdenum from coal firing were of concern due to projected accumulations in vegetation to concentrations that could be potentially injurious to people and to animals.

Scrubbing removed coal-generated sulfate more efficiently than oil-generated sulfate, and 99 percent of coal-fired particles were removed by scrubbing while only 75 percent of oil-fired particles were removed. This may be attributed to the fact that almost 98 (wt) percent of coal-fired particles were greater than 10 μm in diameter whereas the oil-fired particles were smaller. The data suggest the possibility of a net increase across the FGD process in the mass emission rate of particles less than 3 μm in size, and further investigation of this is planned in the CCEA Program. For purposes of comparison, controlled particle emissions for both fuels were well below the old utility boiler New Source Performance Standards (NSPS) of 0.04 g/MJ (0.1 lb/10^6 Btu) of heat input but slightly above the revised limit of 0.01 g/MJ (0.03 lb/10^6 Btu). The results of this study are contributing to the technical basis used by EPA's Office of Air Quality Standards and Planning (OAQPS) in developing NSPS for industrial boilers.

EACCS Project - Environmental Assessment of an 820 MW Coal-Fired Utility Boiler and a 342 MW Oil-Fired Utility Boiler - The CCEA Program has recently completed two studies to characterize multimedia pollutant emissions from utility boilers: one study of an 820 MW coal-fired utility boiler and the other of a 342 MW oil-fired utility boiler. Level 1 and Level 2 sampling and analysis procedures* were used in both cases to characterize emissions in gaseous, liquid, and solid process streams. The major conclusions from each study are presented below.

The coal-fired boiler studied was the No. 1 unit at Kansas City Power and Lights's La Cygne Power Station in Kansas. It typically burns a local high sulfur, high ash subbituminous coal. Sulfur dioxide (SO_2) and particle emissions are controlled by eight venturi/absorber scrubber modules using limestone slurry.

During the study, flue gas was sampled before and after scrubbing. Emissions were determined for the major species, as shown below. Other streams examined were the combined bottom and fly ash, scrubber solids, settling pond overflow, and ash pond overflow.

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* These sampling and analysis procedures are described in a previous CCEA report, EPA-600/7-79-029a, "Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis," (NTIS PB 294675).

The data for total particulate matter emissions indicate 91 percent removal by scrubbing. While scrubber inlet particles were larger than 3 μm in diameter, after scrubbing most particles were less than 1 m in diameter. As was the case earlier for industrial coal combustion, preliminary data suggest an increase in the mass emission rate of particles less than 3 μm in size across the scrubber, and additional CCEA studies are planned to verify or refute this finding.

Some POM compounds were identified at the scrubber inlet, but the levels were considered to be insignificant. The POM compounds identified were naphthalene, substituted naphthalenes, biphenyl, and substituted biphenyls. No POM compound was detected at the scrubber outlet.

The major study conclusions, based on assumed typical and worst case meteorological conditions, are:

- There is a low risk of violating the NAAQS for 24-hour and annual average levels of criteria pollutants. However, units firing high sulfur fuels may exceed the short term NAAQS for SO_2.

- SO_2, $SO_4^=$, and particulate emissions from coal-fired units of the type tested may result in limited adverse health effects, and should be studied further.

- Increased concentrations of cadmium and lead in plant and soil tissues as a result of trace element emissions could cause plant damage and adverse health effects to animals consuming vegetation in the affected areas.

- NO_x and SO_x emissions will probably cause plant damage, since concentrations of both pollutants approach or exceed the damage threshold range.

These conclusions are based on assumed typical and worst case meteorological parameters. Because the environmental acceptability of emissions from coal-fired boilers depends largely on site specific factors, extrapolation from one set of conditions to another should be avoided.

Emissions testing was also performed at the oil-fired No. 5 boiler at Los Angeles Department of Water and Power's Haynes Power Plant in Long Beach, California. This unit is capable of firing either low sulfur oil or natural gas. NO_x emissions are controlled by off-stoichiometric firing and flue gas recirculation. As is typical of oil-fired utility boilers, no particulate or SO_x controls are applied at this site.

The fuel oil and flue gas were analyzed during oil-fired operation. No significant liquid or solid waste streams are produced by the boiler.

Measured emissions of the criteria pollutants and SO_3 (shown below) corresponded well with published emission data from oil-fired boilers (AP-42, NTIS PB 275525), although measured NO_x and total organic emissions were somewhat lower. (The reduced NO_x emissions were the likely result of the NO_x control systems.)

The environmental assessment study concluded that there is a low risk of exceeding the NAAQS as a result of application of this type of boiler. The projected emissions of SO_2, $SO_4^=$, and particles seem to be within acceptable limits. Negligible impacts of trace element burdens on drinking water, plant tissue, soil, and the atmosphere are projected. The risk of damage to vegetation posed by criteria pollutant emissions is remote.

Summary data from the coal-fired tests and the oil-fired tests are presented below.

FLUE GAS EMISSIONS FROM A COAL-FIRED UTILITY BOILER

Pollutant	Emission Factor, ng/J (g/kg) Before Scrubber	 After Scrubber
NO_x (as NO_2 near full load)	$\geq$715 (17.2)[a]	$\geq$385 (9.3)[a]
CO	$\leq$520 (12.5)[b]	$\leq$520 (12.5)[b]
SO_2	3380 ± 400 (81.2 ± 9.6)[c]	740 ± 90 (17.8 ± 2.2)[c]
SO_3	48 ± 24 (1.2 ± 0.6)[c]	10 ± 11 (0.2 ± 0.3)[c]
$SO_4^=$	22 ± 9.0 (0.5 ± 0.2)[c]	2.7 ± 1.9 (0.07 ± 0.05)[c]
Total Organics	2.77 - 4.07 (0.07 - 0.10)[d]	1.45 - 2.60 (0.04 - 0.06)[d]
Total Particulates	1090 ± 270 (26.2 ± 6.5)[c]	80 (1.9)
Cl^-	<0.1 (0.002)	<0.1 (0.002)
F^-	0.6 ± 0.4 (0.014 ± 0.010)[c]	<0.14 (0.003)

---

[a] Measured values are considered to be lower limit values due to potential for NO_x degradation in bag samples.

[b] Determined by GC analysis of bag samples; values represent detection limit of 1000 ppm.

[c] Indicated uncertainty represents one standard deviation.

[d] $C_1 - C_{16}$ fractions determined by GC; $>C_{16}$ fraction determined gravimetrically. Upper limit values include detection limits of fractions which were not found.

EMISSIONS FROM AN OIL-FIRED UTILITY BOILER

Pollutant	Emission Factor, ng/J (g/kg)
NO_x (as NO_2 near full load)	116 ± 2.12 (5.12 ± 0.09)[a]
CO	6.6 ± 3.1 (0.29 ± 0.14)[a]
SO_2	98 ± 7.0 (4.3 ± 0.31)[a]
SO_3	1.14 (0.05)
$SO_4^=$	1.27 (0.06)
Total Organics	0.42 - 0.58 (0.02 - 0.03)[b]
Total Particulates	7.5 ± 1.2 (0.33 ± 0.05)[a]
Cl^-	1.34 (0.06)
F^-	0.061 (0.003)
Cr	0.002 (0.0001)
Ni	0.2 (0.01)

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[a] Indicated uncertainty represents one standard deviation.

[b] $C_1 - C_{16}$ fractions determined by GC; $>C_{16}$ fraction determined gravimetrically.

EACCS Project - Residential and Internal Combustion Sources - As indicated in Section 4, a major project of the CCEA Program is the EACCS project. This project, performed by TRW, Inc., is providing a comprehensive assessment of emissions from several types of conventional stationary combustion processes. The goal of the project is to develop extensive baseline data by identifying and characterizing the gaseous, liquid, and solid pollutants generated by these sources. The final assessment will be based on appropriate existing emissions data as well as on new data acquired through source sampling and analysis.

When the project is completed, assessments will have been made of five major groups of combustion processes:

- Gas- and oil-fired residential combustion sources.
- Gas- and distillate-oil-fired gas turbines and reciprocating engines (internal combustion sources) for electricity generation and industrial application.
- External combustion sources for electricity generation.
- Industrial external combustion sources.
- Commercial/institutional external combustion sources.

Assessments of the first two major groups have been completed, and the final reports are available.

To date, Level 1 sampling has been completed at about 170 sites, and Level 2 sampling has been performed at 15 sites. Two EACCS reports present the results of these efforts for two groups of source categories. "Emissions Assessment of Conventional Stationary Combustion Systems: Volume I: Gas- and Oil-Fired Residential Heating Sources" (EPA-600/7-79-029b; NTIS PB 298494) considers combustion units for space heating with gas or oil input capacities below 0.12 MJ/s (400 Btu/hr). Gas-fired systems and oil-fired systems account for 58 percent and 38 percent, respectively, of residential units. Residential combustion systems consume about 15 percent of the fuel used by conventional stationary combustion systems.

Initially, five gas-fired and five oil-fired residential sources were tested; mass emission rates of criteria pollutants, trace elements, and organics (including POM) were determined. Emission data for particles, $SO_4^=$, SO_3, and SO_2 were also obtained at the oil-fired sites. Later tests were performed at one gas-fired and two oil-fired sites to determine the effect of the boiler on/off cycle on emissions.

Severity factors were calculated for the various species emitted. The severity factors are defined as the ratio of the calculated maximum ground level concentration of the pollutant species to the level at which a potential hazard exists. Concentrations for multiple combustion sources were determined using a dispersion model for an array of 1000 sources.

The study concludes that residential sources are of potential significance based on multiple source severity factors. Multiple source severity factors exceeded 0.05 (the level which may be potentially significant) for NO_x from gas-fired sources and for SO_3, NO_x, and Ni from oil-fired sources. Measured criteria pollutant emission factors were generally comparable to the EPA emission factors based on earlier data (AP-42, NTIS PB 275525), except for total hydrocarbon emissions from oil-fire sources, which were three times greater. POM compounds that were known to be carcinogenic were not found above the detection limit of 0.3 $\mu g/m^3$.

The report recommends additional work to augment the emission data base for oil-fired sources, especially with regard to SO_3 and POM emissions and multiple source severities. The emission data base for gas-fired residential sources is currently considered adequate and no further study is recommended at this time.

The second EACCS report, "Emissions Assessment of Conventional Stationary Combustion Systems: Volume II: Internal Combustion Sources" (EPA-600/7-79-029c; NTIS PB 296390), examines stationary internal combustion (IC) sources for electricity generation and industrial use. The sources are classified as (1) gas- and distillate-oil-fired gas turbines and (2) reciprocating engines (diesel). Six gas turbines (five oil- and one gas-fired) and five distillate oil reciprocating (diesel) engines were tested. The existing data for gas-fired reciprocating engines were judged to be adequate. The data for gas-fired turbines were also considered to be adequate, but one site was included to ensure that previously unidentified pollutants were not being emitted in unacceptable quantities.

Two major conclusions of the study are that:

- IC sources contribute significantly to the national emissions burdens. NO_x, hydrocarbon, and carbon monoxide (CO) emissions from IC sources account for approximately 20, 9, and 1 percent, respectively, of the emissions of these pollutants from all stationary sources.

- Several pollutants emitted by IC sources are of environmental concern. These include NO_x (from all sources examined), total hydrocarbons (from gas reciprocating engines and distillate oil reciprocating engines), SO_x (from distillate oil reciprocating engines), SO_3 (from distillate-oil-fueled gas turbines and distillate oil reciprocating engines), and trace elements (from most of the oil-fueled IC sources tested).

Source Assessment Project - Dry Bottom Industrial Boilers Firing Pulverized Coal - The primary method of coal combustion in U.S. industrial boilers is in dry bottom units firing pulverized bituminous coal. A multimedia environmental assessment of this source type was recently completed by Monsanto Research Corporation for EPA (EPA-600/2-79-019e; NTIS PB 80-177207). The study, "Source Assessment: Dry Bottom Industrial Boilers Firing Pulverized Bituminous Coal," was based on an extensive literature search and sampling and analysis as well. It concludes that certain air emissions are released at potentially hazardous concentrations even when existing controls are applied. The potential impacts of controlled liquid and solid waste discharges from this source, however, are insignificant.

Dry bottom boilers operate at temperatures below the ash fusion temperature. Ash remaining in the bottom of the furnace is removed as a dry powder. Most of these boilers are in the industrialized Northeast states, in large cities and along major waterways. This source category represents about 9 percent of the total steam-generating capacity of U.S. industry and approximately 49 percent of the industrial steam generated by coal combustion. The average capacity of the industrial boilers considered in this assessment was 222 GJ/hr (2.1×10^8 Btu/hr).

More than 99 percent of the air emissions result from coal combustion in the furnace and are emitted from the boiler stack. Major emissions are the criteria pollutants: particles, SO_x, NO_x, hydrocarbons, and CO. POMs are among the hydrocarbon species emitted. In addition, trace elements are released as part of the particulates or in the vapor phase.

The potential environmental impact of each species emitted after passing through state-of-the-art controls was individually assessed on the basis of source severity. Source severity, an indicator of potential environmental impact, is the ratio of the maximum ground level concentration to a potentially hazardous concentration. Species with source severities greater than 1.0 were NO_x (1.7), SO_x (2.2), and POMs (6.0).

Dispersion modeling was applied to determine the affected population, defined as the population exposed to specified potentially harmful emission levels from an average source. Estimates of the number of persons exposed to severities greater than 1.0 are shown below.

Emission Species	Source Severity*	No. of Affected Persons
NO_x	1.7	1,200
SO_x	2.2	2,200
POM	6.0	7,500

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* Ratio of the maximum ground level concentration to a potentially hazardous concentration

The study predicts that the total design capacity of boilers covered in this assessment will increase at an annual rate of 3 to 4 percent through 1990. Total air emissions and wastewater effluents during this period will likely remain constant or drop slightly due to increased controls. The volume of solid wastes is expected to grow as air emission controls are increasingly applied to this expanding source.

Source Assessment Project - Residential Coal Combustion - Some regions of the U.S. show a trend toward increased home heating with coal. A recent study conducted by Monsanto Research Corporation characterized the emissions from residential coal combustion and evaluated their potential environmental effects. The study results are presented in the final report, "Source Assessment: Residential Combustion of Coal" (EPA-600/2-79-019a; NTIS PB 295649).

In 1974 approximately 2.6 Tg (2.9×10^6 tons) of coal were burned as a primary source of heat in an estimated 493,018 housing units. Although this represents only 1 percent of the total U.S. housing units with primary heating devices, interest in this form of heating is growing. From 1972 to 1975, sales of domestic coal-fired heating stoves increased by 130 percent. Since 1976, sales of other heating devices such as stoker furnaces have also increased. With the current shortages of natural gas and oil, these trends may continue for some time, a likelihood that underscores the importance of assessing coal-fired home heaters.

Coal-fired residential combustion sources consist of all equipment that burns bituminous, anthracite, or lignite coal to generate household heat. These devices produce up to 0.12 MJ/s (4.0×10^5 Btu/hr) of heat in occupied structures containing one or two housing units. A wide variety of primary residential coal-fired heating equipment is available; common types include steam or hot water boilers, warm air furnaces, and domestic heating stoves.

Residential coal combustion generates many atmospheric emissions in addition to a solid residue. Atmospheric emissions include particles, SO_x, NO_x, CO, hydrocarbons (including POMs), and trace elements. Pollutants are generated during the combustion process and, with the exception of some of the NO_x, are formed from the coal as it burns. Some NO_x is formed by the combination of atmospheric nitrogen and oxygen at high temperatures in the furnace.

The solid residue consists of inert material (ash) and unburned or partially burned fuel. If the solid residue is disposed of by landfill, elements may be leached out by rainfall into water supplies.

Unlike larger combustion systems such as utility boilers, which have tall stacks to disperse emissions and reduce ground level concentrations, residential units emit pollutants close to ground level where dispersion is minimal. In addition, several residential coal combustion sources may be concentrated in a small area, such as a housing subdivision. In these cases, an additive multiple source effect resulting in increased ground level concentrations could occur.

The study evaluated the potential environmental effects of air emissions from coal-fired residential combustion systems on the basis of source severity, affected population, state emission burdens, and national emission burdens.

The source severity measures the potential health effect of a pollutant at its maximum ground level concentration. Generally, 0.05 is considered a threshold level, above which a potential environmental problem may exist. An average combustion unit was determined for each coal type as a basis for severity calculations. (For instance, an average bituminous coal-fired unit burned Appalachian coal at the rate of 0.3 g/s (11 tons/year) and was located in an area with an average population density of 132 persons/km^2.) POM emissions showed a severity of 2.6 for bituminous coal combustion, while severities of the other emissions were 0.05 or less.

An assessment of the environmental impact of composite emissions from 100 houses burning coal indicated the potential for a thirtyfold increase in the associated severities. Severities were greater than 0.05 for 16 individual elements and 4 criteria pollutants (particles, SO_x, NO_x, and hydrocarbons). Severities were 91 and 1.7 for POM in bituminous and anthracite coal burning, respectively.

POM was the only pollutant from a single source projected to have a potential effect on the exposed population. However, the potential effect on the exposed population of pollutants from multiple residential combustion sources was much greater than the effects from a single source. Multiple source emissions of particulates, SO_x, NO_x, hydrocarbons, 16 individual elements, and POM showed severities greater than 0.05.

The study determined the contributions of coal-fired residential combustion to state and national levels of criteria pollutant emissions. In 1974 home heating with bituminous coal had the greatest impact on a state-by-state basis, exceeding 1 percent of the total state SO_x emissions in the District of Columbia, Virginia, and West Virginia. Criteria pollutant emissions from anthracite and lignite combustion were all less than 1 percent of the total state emissions in every state.

While the criteria pollutant annual emissions from residential coal combustion comprise a relatively small fraction of the total annual emissions of these pollutants, the levels of POM released may be significant. In 1974 the national annual emissions of POM totalled about 101 Mg (111 tons) from automatic bituminous-fired units and about 0.9 Mg (1 ton) from automatic anthracite-fired units. This represents approximately 10 percent of the total annual estimated national emission of POM from all stationary sources (industrial, residential, commercial/institutional, and utility).

Emissions from residential combustion systems are not typically controlled with add-on equipment but can be reduced by improved design and proper operation. Factors to be considered include fuel properties and type, firing rate, firing equipment design, cyclic operation of automatic equipment, and excess air ratios.

CCEA Systems Engineering Project - Volatile Organic Compound (VOC) Emissions - A recent CCEA study has provided updated volatile organic compound (VOC) emission factors for utility coal-fired power plants in support of the Monitoring and Data Analysis Division of EPA's Office of Air Quality Planning and Standards (OAQPS). OAQPS is responsible for developing the reactive VOC emission factors, which will be used by the Regions and States in meeting Prevention of Significant Deterioration (PSD) requirements.

The VOCs analyzed in the study were C_1 to C_{16} hydrocarbons. Level 1 procedures were used to test for stack VOC emissions from 43 utility boilers firing bituminous coal, lignite, residual oil, or gas. Boiler size ranged from a small lignite-fired boiler of 9 MW to a large bituminous coal-fired unit of 910 MW.

Major conclusions of the study were:

- Reactive VOC emissions ranged from 1.7 to 5.1 ng/J (4.0 to $11.9\ lb/10^9$ Btu) heat input.
- Bituminous-coal- and lignite-fired boilers emitted 1.2 to 3.0 times more VOCs than did residual-oil- and gas-fired boilers.
- Of total reactive VOCs, 85 to 95 percent were due to the C_2 to C_6 hydrocarbon group.
- There was no appreciable difference in the quantities of VOC emissions from bituminous-coal- and lignite-fired boilers. Similarly, there was little quantitative difference between residual-oil- and gas-fired boiler VOC emissions.

- The reactive VOC emission factors and annual reactive VOC emissions are accurate within a range of ± 200 percent, which is consistent with IERL-RTP Level 1 requirements.

The study recommends further testing with Level 2 sampling and analysis procedures to determine quantities of oxygenated hydrocarbons. Also suggested is the use of a statistically designed experimental matrix to evaluate the effects of boiler types and boiler operating parameters on VOC emissions.

EACCS Project - POM Emissions from Industrial Wood Combustion - Preliminary results from CCEA field testing at five industrial wood-fired boilers indicate that wood combustion produces substantially more emissions of POM than other source categories. Field tests, performed by TRW, Inc., found average POM emissions from the five industrial sites to be 0.8 mg/m^3. This value is 80 times greater than the average POM emissions determined for utility boilers firing bituminous coal, and 133 times greater than those found for lignite-fired utility boilers.

POM emissions from these industrial wood-fired boilers are not only high, but also include emissions of such highly carcinogenic compounds as:

- benzo(a)pyrene
- benzo(e)pyrene
- dibenzo(a,h)anthracene
- dibenzo(def,mno)chrysene
- benzo(g,h,i)perylene
- indeno(1,2,3-cd)perylene

In view of the potential magnitude and severity of these emissions, additional sampling and analysis are underway to substantiate these preliminary findings. Once the extent of the problem has been clearly defined, the CCEA Program will recommend an approach for dealing with it.

Source Assessment Project - Residential Wood Combustion - A recent EPA report, "Preliminary Characterization of Emissions from Wood-Fired Residential Combustion Equipment," presents results from a comprehensive study undertaken to characterize emissions from residential wood-burning devices. The report, EPA-600/7-80-040 (NTIS PB 80-182066), prepared for the CCEA Program by Monsanto Research Corporation, focuses on the effects of certain test parameters on pollutant species. Conclusions show that combustion equipment design influences certain emissions. Levels of CO and POM were highest from wood-burning stoves, while NO_2 emissions were greatest from fireplaces. The effect of wood type was also studied, and results showed increased levels of organic compound emissions from the combustion of green pine.

In this preliminary study of residential wood combustion, one fireplace and two wood-burning stoves were tested during the combustion of four types of wood (green and seasoned yellow pine and red oak). Gaseous emissions were sampled and analyzed for particulates, condensable organics, SO_2, NO_2, CO, organic species (including POM), and individual elements. Bioassay tests were also conducted on the stack emissions and bottom ash. Samples were collected at Auburn University (Auburn, Alabama) during March and April 1979.

The three combustion units tested during this study were a residential fireplace, a baffled wood-burning stove, and a nonbaffled wood-burning stove. Because the emphasis is now on energy efficiency, airtight metal stoves, which are claimed to be 50 to 70 percent energy efficient, are becoming very popular. Baffled stoves are generally more sophisticated in design than nonbaffled stoves and are designed to improve combustion efficiency by providing longer retention time, a secondary combustion zone, and secondary combustion air. Fireplace design, however, favors more complete combustion because the combustion air is not as restricted as it is in wood-burning stoves. Indeed, examination of the wood-burning rate revealed that wood was consumed in the fireplace at a rate 40 percent greater than in the stove, evidence of a hotter fire and better combustion.

The two stoves had similar emissions, but differences were noted between stove and fireplace emissions. CO and POM emission factors were an order of magnitude higher from the stoves than from the fireplace, as shown below in the data obtained during combustion of seasoned oak:

Equipment	CO Emission Factor g/kg	POM Emission Factor g/kg
Fireplace	30	0.025
Baffled Stove	110	0.21
Nonbaffled Stove	370	0.19

Since both CO and POM are products of incomplete combustion, they are expected to be emitted in greater amount under the poorer combustion conditions of the stove.

The data on particulate matter and hydrocarbon emissions were highly variable, and no trends were noted in the emissions of these species. It is unclear why particulates and hydrocarbons did not exhibit higher emission factors from the stoves, since they too form as a result of incomplete combustion.

NO_2 emissions from the fireplace were approximately four times greater than NO_2 emission from the stoves. Since NO_2 emissions depend primarily on combustion temperatures (as long as sufficient excess air is present for complete combustion), it is not surprising that higher NO_2 emission factors occurred during the fireplace tests where hotter temperatures prevailed.

No significant differences were noted in emissions between the two airtight stoves tested. The baffled stove, despite its design, did not increase combustion efficiency, as evidenced by the similar emission factors and energy efficiencies of both stoves.

The data obtained are in general agreement with other studies of this source type. Caution should be exercised, however, in extrapolating these results to other test conditions. Further studies are recommended to provide information on such variables as wood geometry, firing rate, and air/fuel ratio.

Source Assessment Project - NO_x Emissions from Wood-Fired Industrial Boilers - Results from a CCEA study performed by TRW, Inc. (EPA-600/7-79-219; NTIS PB 80-102288) indicate that wood-fired boilers emit considerably less NO_x (on an energy basis) than fossil fuel boilers of comparable size. The study, "NO_x Emission Factors for Wood-Burning Boilers," points out that this conclusion is not expected, since most wood-fired boilers operate with high levels of excess air, a practice normally associated with increased NO_x emissions.

These findings are based on source test data obtained from 14 industrial boilers firing either wood alone or in combination with oil, coal, or natural gas. The types of fuel woods studied were mostly wood processing residues, such as sawdust, chips, shavings, edgings, bark, and scraps. The boilers tested ranged in size from 1.5 to 67 MW (4,450 to 200,000 lb steam/hour).

Test data for each source were used to determine NO_x emission rates in the units of g/kg fuel and mg/MJ. The boilers were then separated into three size categories, on the basis of the mean emission rates within the categories.

Emission factors are shown below, based on the test data from boilers in each size category. Most of the large wood-fired boilers are co-fired with a conventional fossil fuel. Although this study focused on boilers which use wood as the primary fuel, emissions data from these co-fired systems were included in the development of emission factors. A separate emissions factor was developed for boilers firing wood as a minor supplement to coal.

Boiler Size	g NO_x/kg Fuel	mg NO_x/10^6 joule
<10.0 MW	0.03	9.0
>10.0 MW	1.60	70.0
>10.0 MW*	4.00	170.0

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* Wood used as supplement to coal

The unexpected finding that NO_x emissions from wood-fired boilers generally decrease with higher levels of excess air can be explained by the fact that, in wood-fired boilers, high levels of excess air reduce the fire box temperature. This in turn decreases the rate at which thermal NO_x is formed. (Thermal NO_x is the NO_x formed by oxidation of atmospheric nitrogen in the combustion air.)

The study found a definite correlation between emission rate and boiler size. Emission rates for boilers smaller than 10 MW (29,670 lb steam/hr) are quite similar. This is not surprising in view of the uniform operating parameters of these smaller boilers. Most operate with more than 300 percent excess air. In addition, fire box temperatures generally range from 1000 to 1100°C (1832 to 2012°F). Larger boilers (greater than 10 MW) exhibit less consistency in operating parameters and emission rates. Excess air use ranges from 62 to 155 percent, and the fire box temperatures are unknown.

6. CONCLUSION

With conventional fuel combustion processes, principally coal combustion, playing an increasing role in our movement toward national energy independence, there is a simultaneous increase in the potential for adverse environmental impacts. The preceding examples of field study data and assessment results are representative of the extensive activities currently underway in the CCEA Program to ensure that the country can increase its reliance on conventional combustion processes at reasonable economic, energy, and environmental costs. The results of the CCEA Program efforts, then, will be recommendations for control technology and support for standards development to control adverse effects within acceptable limits.

GLOSSARY

Discharge Severity - An indicator of potential environmental impact; the ratio of the measured concentration of a pollutant in a discharge stream to a potentially hazardous concentration

EACCS - Environmental Assessment of Conventional Combustion Systems

FGD - Flue Gas Desulfurization

GC - Gas Chromatograph(ic)

NAAQS - National Ambient Air Quality Standards

NO_x - Generic formula for oxides of nitrogen; includes NO and NO_2

OAQPS - (EPA's) Office of Air Quality, Planning, and Standards

POM - Polycyclic Organic Matter

Source Severity - An indicator of potential environmental impact; the ratio of the maximum ground level concentrations resulting from a source to a potentially hazardous concentration

COMBUSTION MODIFICATION
ENVIRONMENTAL ASSESSMENT

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ABSTRACT

The Combustion Modification Environmental Assessment (CMEA) was started in 1976 as part of the Environmental Protection Agency's (EPA) Conventional Combustion Environmental Assessment Program. The primary CMEA objectives are to:

- Identify potential multimedia environmental hazards from stationary combustion sources before and after the use of combustion modifications to control NO_x and other combustion-related pollutants
- Develop combustion modification application guidelines documenting the economic, energy, operational and environmental impacts of meeting prescribed emission levels
- Identify the most cost-effective and environmentally acceptable combustion modification techniques to achieve and maintain environmental goals for NO_2

To support these objectives, the emphasis in the CMEA is on field tests to quantify changes in emissions, energy efficiency, and operation due to the use of combustion modifications. The field testing uses the EPA environmental assessment "Level 1" protocol which includes sampling and analysis for NO_x, SO_2, SO_3, CO, CO_2, O_2, trace metals, organics, and trace inorganic species. During the first 3 years of the CMEA, field tests were done on three utility boilers, two industrial boilers, a gas turbine, and a residential warm air furnace. Each source was either modified in the field for low NO_x operation or was equipped with low NO_x designs. Test results showed no major increase in emissions due to combustion modifications. Changes in emissions other than NO_x were

typically within the accuracy of the experimental methods, or within the range of changes due to day-to-day variations in fuel composition or unit operation.

Changes in the severity to the environment of total source effluents was secondary to the improvement due to NO_x reduction. Energy efficiency was generally unimpared or improved through the use of combustion modifications. One exception was a water injection equipped gas turbine for which a 2 percent efficiency decrease was observed.

The CMEA program has recently been renewed to extend the field test program to additional sources, advanced combustion modification controls, alternate fuels, and nonsteady operation. The site selection and field test status for the extended program are described.

SECTION 1

INTRODUCTION

In 1975, EPA's Industrial Environmental Research Laboratory (IERL) started a major program for the environmental assessment of energy systems and industrial processes. The purpose of these assessments is to detect and quantify potential environmental problems with the systems or processes and identify potential control measures to reduce the environmental problems found. This information is needed by EPA and other agencies to establish R&D priorities, to support standards setting activities by regulatory groups, and to develop environmentally acceptable energy systems.

Environmental assessments of stationary conventional combustion sources are coordinated by the "Conventional Combustion Environmental Assessment" (CCEA) program managed by IERL-Research Triangle Park (RTP). A major component of the CCEA is the CMEA. The CMEA was started by IERL-RTP's Combustion Research Branch in June 1976 to support the overall EA program by focusing on stationary combustion sources with combustion modification techniques to control NO_x or other pollutants amenable to control through combustion process modification.

The three primary objectives of the CMEA are to:

- Identify potential multimedia environmental hazards from stationary combustion sources
  - Under baseline operation without combustion modification controls
  - Under controlled operation to suppress NO_x or other pollutants amenable to control through combustion process modification
- Develop control application guidelines on the economic, energy, and operational impacts of meeting prescribed emission levels

- Identify the most cost-effective and environmentally acceptable NO_x control techniques to achieve and maintain air quality considering:
  - -- Current and anticipated air quality standards
  - — Alternate equipment use and fuel use scenarios to the year 2000

The program approach to address these objectives is illustrated in Figure 1. Here, the rectangles denote major tasks while the ovals denote outputs. The flowchart at the left of Figure 1 shows the approach for the first two objectives, while the approach for the third objective is shown by the flowchart at the right.

Since 1976, the CMEA program objectives have been accomplished for the major stationary sources firing conventional fuels and equipped with conventional combustion modifications. The overall results from the initial 3-year effort are summarized in Reference 1. The emission characterization effort shown in Figure 1 was documented in References 2 and 3 and updates were supplied in References 1 and 4. The test program results are summarized in a series of test reports, References 5 through 11, which will be available through the National Technical Information Service in the fall of 1980. The process engineering and impact analysis results are documented in a series of source-specific reports for utility boilers, industrial boilers, gas turbines, residential heating systems, and internal combustion engines (12 through 16). The preliminary air quality analyses to identify combustion modification R&D priorities were initially documented in Reference 17. These analyses were subsequently updated in References 1 and 4 using current regulatory policy and NO_x control technology information.

The CMEA has recently been extended to augment the initial results by evaluating more advanced control technologies, secondary NO_x sources, alternate fuels, and nonsteady operation. Although the emphasis in the extended program is on field testing, the other program elements in Figure 1 will be updated as more current information becomes available.

This paper presents the field test program results from the first 3-year effort and summarizes the plans for the first year of the extended program. Section 2 describes the sources tested and the sampling and analysis protocols used in the initial field test program, and Section 3 presents the results. The site selection and field testing for the extended program are reviewed in Section 4.

SECTION 2

INITIAL TEST PROGRAM

The purpose of the CMEA test program is to quantify how source emissions, efficiency, and operation are affected by combustion modification techniques. To help formulate the test program, a preliminary environmental assessment (17) was conducted during the first year of the CMEA. This assessment surveyed available data, identified data gaps, and set priorities on sources, fuels, and controls for the initial CMEA effort. The assessment showed a virtual absence of data on the effects of combustion modifications on noncriteria flue gas pollutants and on solid or liquid effluents. The assessment concluded that comprehensive field tests were needed to show the effects of combustion modifications on vapor phase hydrocarbons, particulate load and size distribution, sulfur species, vapor and condensed phase trace elements, and vapor or condensed phase organic species. The preliminary assessment further concluded that priority in the initial field tests should be on major source categories, conventional fuels, and conventional combustion modification techniques.

Based on the results of the preliminary source/control priorities established in the first year of the CMEA, 19 candidate field tests were identified. From the 19 potential tests, seven were selected and tested. A summary of these seven tests is given in Table 1. Where possible, the CMEA tests were done as an augmentation to ongoing tests done as part of other programs.

The test plan developed for each test called for sampling all influent and effluent streams with the exception of the ambient air. Continuous monitors were employed to measure flue gas NO_x, CO, CO_2, and O_2. EPA Level 1 procedures (18, 19) were used to sample the flue gas and all discharge ash streams for trace element and organic species. In addition, flue gas particulate and sulfur species concentrations were measured in each test. Flue gas sampling upstream and downstream of particulate collection devices were always performed. An example of the samples collected during a test are shown in Figure 2. Operating data sufficient to calculate unit efficiency, cycle efficiency, and verify consistent operation, were also recorded.

For each test the following environmental assessment sampling protocol was used:

- Continuous monitoring of flue gas NO_x, CO, CO_2, and O_2 (SO_2 was only measured continuously during one test)
- Flue gas Source Assessment Sampling System (SASS), EPA Method 5 particulate load, and EPA Method 8 (or equivalent) sulfur species sampling; both upstream and downstream of the particulate collector, if applicable
- Flue gas grab sampling and onsite gas chromatographic analysis for C_1-C_6 hydrocarbons; both upstream and downstream of the particulate collector, if applicable
- Bottom ash slurry sampling
- Particulate collector hopper ash sampling
- Fuel and fuel additive if applicable sample collection,
- Operating data collection

As noted in Table I, the test program was conducted, at a minimum, for at least two conditions of source operation: baseline (uncontrolled), and low NO_x operation. In several instances, operation at intermediate levels of NO_x control was tested. In addition, replicate testing was performed in selected cases.

A key part of the test program involved close monitoring of source operating data. This was done not only to ensure that test conditions remained constant and representative of acceptable source operation over the duration of sample collection, but also to provide the necessary input to further process analysis efforts.

Laboratory chemical analyses of samples collected generally followed IERL-RTP defined Level 1 procedures (18, 19) with a few exceptions and additions. Level 1 is a semiqualitative screening approach used in environmental assessments to identify areas needing further analysis. A simplified schematic of the analysis scheme adopted for SASS train Level 1 samples is illustrated in Figure 3. The analysis scheme for solid (ash) samples and the general organic analysis scheme is described in Reference 1.

A specific exception to the Level 1 protocol dealt with sample trace element analysis. Here, instead of assaying for trace elements by spark source mass spectrometry, atomic absorption spectroscopy was employed to determine the 25 more commonly occurring elements listed in Table II. Another exception dealt with organic analyses of flue gas (XAD-2 extract), particulate, and liquid/solid samples. Here the analyses were extended, when feasible, to the determination of polycyclic organic compounds (POM) and later to the determination of the priority pollutant compounds listed in Table III.

Following the procedures of the Level 1 analysis, data listed below can be obtained for each test point:

- Continuous flue gas NO_x, CO, CO_2, and O_2
- Flue gas SO_2, SO_3 and speciated C_1-C_6 hydrocarbons
- Flue gas particulate load and size distribution
- Flue gas vapor phase trace element composition for the 25 elements listed in Table II
- Flue gas $>C_7$ organic composition in terms of seven compound polarity fractions and flue gas composition for the species listed in Table III
- Particulate composition for the 25 elements listed in Table II and the six ionic species listed in Table IV, as a function of particulate size
- Particulate organic composition in terms of seven polarity fractions, and for the species listed in Table III, as a function of particulate size
- Liquid/solid stream (bottom, hopper ash) composition for the 25 elements listed in Table II and the six ionic species listed in Table IV
- Liquid/solid stream (bottom, hopper ash) composition for seven polarity fractions and for the species listed in Table III

- Particulate and ash combustible material content
- Fuel proximate and ultimate analysis (heating value, and water, C, H, O, N, and S content)
- Fuel trace element content for the 25 elements listed in Table II

The above data satisfy the specific CMEA program needs identified. Specific attention was focused on obtaining data on emitted POM, SO_3 and condensed sulfate, and trace element levels as a function of particulate size, especially as these are affected by combustion modification NO_x control applications.

Bioassay testing in accordance with IERL-RTP guidelines (20) was performed on samples collected during the gas turbine, Crist Unit 7, Site B, and the Moss Landing Unit 6 tests. The bioassays are conducted on samples collected during the controlled (for NO_x) tests only. The general Level 1 bioassay protocol for the CMEA tests is given in Table V. This test protocol includes both health effects and ecological effects tests. However, sample size requirements for certain tests are substantial. Thus performing certain tests was often precluded. The actual bioassays performed in the test program are listed in Table VI.

SECTION 3

TEST RESULTS

Detailed sampling and analysis results from the initial test program are documented in References 5-11. For this paper, the results will be represented in terms of the Source Analysis Model (21). The Source Analysis Model compares discharge stream specie concentrations to threshold concentrations of these species. For the purposes of screening pollutant emissions data to identify species requiring further study, a discharge severity (DS) is defined as follows:

$$DS_i = \frac{\text{Concentration of Pollutant i in Effluent Stream}}{\text{Discharge Multimedia Environmental Goal}}$$

The discharge multimedia environmental goal (DMEG) values describe maximum concentrations believed to be safe for short-term direct exposure to a discharge stream (21). The DMEGs are used in EPA's environmental assessment programs to indicate when a specie concentration is sufficiently high to warrant further evaluation. Stream discharge severity is evaluated as the sum of the individual specie discharge severities.

To compare waste stream potential hazards, a weighted discharge severity (WDS) is defined as follows:

$$WDS = (\Sigma_i \, DS_i) \times \text{Mass Flowrate},$$

where the discharge severity is summed over all species analyzed. The weighted discharge severity is an order of magnitude indicator of hazardous pollutant release and can be used to rank the needs for controls for waste streams. It can also be used as a preliminary measure of how well a pollutant control, say a combustion modification NO_x control, reduces the overall environmental hazard of the source.

Tables VII and VIII present a summary of the CMEA test results noting the pollutants of concern. The tables show pollutant components with discharge severity (DS) values greater than 1 for any source tested, with an indication of the magnitude of the discharge severity for each component for each source. Table VII presents results for the flue gas stream; Table VIII for the ash streams.

From Table VII, it is apparent that SO_2 and NO_x emissions present the greatest potential hazard from all the combustion sources tested. The discharge severity for these is especially high from coal-fired sources. Other species with high discharge severity in most tests include CO_2, CO, As, and SO_3 (vapor phase). The only organic emissions of potential concern noted were those of carboxylic acids; though this would be so only under the conservative assumption that all the organics analyzed in SASS train catches consisted of the most toxic carboxylic acid on the DMEG list; maleic acid. Even so, the discharge severity values are only of order 1. Several other trace element species and condensed sulfate were flagged of concern in several tests, though these were not universally noted.

Table VIII shows that the potentially most hazardous species in the ash streams from coal-fired sources were iron and manganese, followed by chromium, nickel, beryllium, and barium. Interestingly, lead levels were high only in particle collector ash streams, particularly the ESP hopper ash, suggesting that lead partitions to potentially hazardous levels on passage through a boiler.

Table IX compares the stream discharge severities. The stream discharge severities for a given source are generally within an order of magnitude of each other. In Table X, the stream discharge severity is weighted by the stream flowrate. It is clear that the flue gas stream dominates the effluent streams.

General conclusions that can be derived from the SAM IA discharge severity evaluations include:

- NO_x and SO_2 represent the potentially most hazardous flue gas species from the sources tested; the sum of the discharge severity values for these two species in general accounts for greater than half the stream discharge severity

- The flue gas stream weighted discharge severity dominates the source total weighted discharged severity for sources which discharge other (ash) streams (coal-fired sources)
- NO_x control application either reduces flue gas discharge severity and weighted discharge severity, or, at worst, does not increase these; this translates to a reduction, or, at worst, no increase in source total weighted discharge severity
- In general, changes in flue gas discharge severity and weighted discharge severity due to NO_x control are less significant than those resulting from day-to-day variations in fuel composition (especially sulfur)

Carbon Monoxide and Vapor Phase Hydrocarbons

The presence of CO and vapor phase hydrocarbons (HC) in the exhaust gases of combustion systems results from incomplete fuel combustion. The various combustion modification controls tested can give rise to conditions resulting in incomplete combustion, so increased emissions of CO and HC can be a concern in NO_x control application. However, since emissions of CO and HC are associated with decreased efficiency, combustion sources are generally operated, even with NO_x control, to keep these emissions at a minimum. The preliminary environmental assessment (17) concluded that increased emissions of these due to combustion modification control should not be considered a major concern. Results of the CMEA test program substantiate this.

Table XI shows CO and HC emissions as a function of NO_x control application for the tests performed. As noted in the table, emissions of these either remain relatively unchanged or increase only slightly with the combustion modifications tested.

Particulate and Particle Size Distribution

The preliminary environmental assessment (17) concluded that the effects of combustion modification controls on particulate emissions, and especially on emitted particle size distribution, from stationary sources had been insufficiently studied. Further, since NO_x controls can produce combustion conditions conducive to increasing particulate emissions, this was flagged as an area of potential concern.

The data obtained in the CMEA test program on particulate emissions are summarized in Table XII. The table shows that particulate emissions generally remain unaffected, or are decreased slightly with the NO_x control applications tested. Particle size distribution data taken for the coal-fired sources also showed that emitted particle size distribution remained unaffected or increased slightly (5, 7, 8, 10).

Trace Element Emissions

The preliminary environmental assessment (17) concluded that the effects of NO_x control application on emissions of trace elements, both segregating (those which tend to partition to fine particulate) and nonsegregating (those which tend to remain equally distributed with particle size in ash), should be marginal. However, the preliminary assessment noted that few data existed to substantiate that conclusion.

The data obtained in the CMEA test program, however, do indicate that combustion modification controls have no measurable effect on trace element emissions. The test program shows that, within analytical uncertainties, trace element levels in flyash, bottom ash, and particulate collector hopper ash streams remain generally unchanged as a function of NO_x control application.

In addition, data presented in References 5, 7, 8 and 10 also indicate that:

- Trace element partitioning to fine particulate occurs in accordance with expectations (17), but
- Changes in trace element partitioning tendencies with combustion modifications are undetectable

SO_3 and Sulfate Emissions

High ambient sulfate levels are currently a matter of great concern in regions of the U.S. with large numbers of combustion sources firing sulfur bearing coal and oil. The primary reason for this concern is that increasing ambient sulfate levels are contributing to the problem of acid precipitation, particularly in the northeast U.S., but in other parts of the country as well. Ambient sulfates are comprised of directly emitted, or primary, sulfates and those derived from the atmospheric oxidation of SO_2, or secondary sulfates. Although the relative contributions to ambient sulfate levels from each of these is undetermined, it is clear that an increase in primary sulfate emissions should be viewed with concern.

Combustion modification NO_x control would be expected to either reduce or leave unchanged the emissions of primary sulfates from combustion sources. Such was the conclusion of the preliminary environmental assessment (17). However, the preliminary assessment also noted that few data to substantiate this conclusion existed, thus obtaining such data was given priority.

Table XIII shows the flue gas SO_3 and particulate sulfate data taken during the test program. Also shown is the weight fraction of sulfur emitted as SO_3 and $SO_4^=$, expressed as the ratio $(SO_3 + SO_4^=)/(SO_2 + SO_3 + SO_4^=)$. The table shows that the fraction of sulfur emitted as SO_3 and particulate sulfate varies from just under 1 percent for coal-fired sources to 5 to 10 percent for oil-fired sources, in agreement with previous data (22). The table also shows that the fraction of sulfur emitted as $SO_3 + SO_4^=$ remains relatively constant, or decreases slightly with NO_x control application.

Polycyclic Organic Matter and Other Organic Emissions

Just as combustion modification controls have the potential for increasing CO and HC emissions due to decreased combustion efficiency, emissions of other organic species can potentially increase also. Since few data existed on the effects of NO_x control on combustion source POM and other organic emissions, and since several species in this pollutant class are quite hazardous, priority was given to obtaining data on these emissions in the CMEA test program.

Table XIV shows total SASS train organic determination data for the tests performed. Infrared analysis of sample extracts showed the organic species in the samples were in the aliphatic hydrocarbon, ether, ester, aromatic, and carboxylic acid categories. The data in the table indicate, though, that as was the case for CO and HC emissions, emission of these higher molecular weight organics remain relatively unchanged with NO_x control application. The seemingly high levels of organic compound emissions in the Blueray residential furnace test are primarily unburned

191

fuel oil. This was a result of the "on-off" cycling of the furnace during the test.

Table XV shows the results of the Gas Chromatography/Mass Spectrometry (GC/MS) analysis of SASS train samples for the tests for which the analysis was performed. In all these tests at least 11 POM species were screened. For the Crist Unit 7 and Moss Landing Unit 6 tests the POM species and organic priority pollutants listed in Table III were analyzed.

Table XV shows that there is a marginal increase in POM emissions with NO_x control application. The emissions levels were generally in the order of the detection level of the instrument. It is interesting to note that, in the Crist and Moss Landing analyses for the organic priority pollutants, none of the organic priority pollutants were found within the detection limits.

Bioassay Results

Bioassay testing of samples taken during the Crist Unit 7, Moss Landing Unit 6, Site B and gas turbine lowest NO_x tests was performed in the test program. Table XVI summarizes results from all the bioassay tests performed and notes the stream total discharge severity for the appropriate sample assayed. However, from the data presented in the table no real correlation between stream discharge severity and bioassay test results is apparent. The fact that most bioassays gave nondetectable toxicity responses frustrates deriving any correlation.

SECTION 4

CURRENT TEST PROGRAM

The initial test program was based on filling priority data gaps identified early in the CMEA. The identification of these data gaps led to the testing of major source categories, conventional fuels, and conventional combustion modification techniques. In the current test program, these source categories will continue to be evaluated. In addition, the following priorities will be addressed:

- Advanced NO_x controls
  - Evaluation of controls with regard to the impending New Source Performance Standard (NSPS)
  - Evaluation of controls designated Best Available Control Technology (BACT)
- Alternate fuels
- Secondary sources
- CCEA Program data needs
  - Residential oil combustion
  - Wood firing in residential, commercial, and industrial sources
  - High interest emissions determinations (dioxins, radionuclides, etc.)
- Nonsteady state operation

As in the initial program, operating data and emissions data will be evaluated to determine the overall effects of combustion modification controls.

The goal of the current program is to test approximately ten sources per year. Whenever possible, cooperative test efforts with other contractors will be encouraged so that the available data base will be enhanced.

At this time four field tests in the current program have been completed. The sources tested were two stationary reciprocating internal combustion engines (one spark ignition and one compression ignition) and two low emission distillate oil-fired residential furnaces. These sources are described in Table XVII. Other test programs currently scheduled for this year include a pulverized coal-fired utility boiler designed to meet the 1971 NSPS, a small wood-fired industrial boiler, two industrial combustion sources equipped with noncatalytic ammonia injection systems, a process heater equipped with advanced staged combustion for NO_x control, and a coal-fired industrial stoker with coal limestone pellets for SO_2 control. Results of these programs will be available in individual test reports under the CMEA program. Additionally, an annual report will be available in spring 1981 summarizing the program results.

SECTION 5

SUMMARY

The CMEA field tests conducted to date indicate that:

- For the sources tested, the flue gas stream presents the greatest potential environmental hazard
- NO_x and SO_2 are the potentially most hazardous flue gas pollutants
- Flue gas discharge severity is decreased or, at worst, does not increase with applying the combustion modifications tested; changes in emissions due to day-to-day fuel composition changes are often of greater magnitude than those attributable to NO_x control
- The effluent streams from the sources tested are not mutagenic, and, in general, elicit nondetectable toxicity in bioassay testing
- The combustion modifications tested:
  - -- Have no effect, or increase only slightly, emissions of CO and vapor phase hydrocarbon
  - -- Have no effect on particulate mass emissions
  - -- Have no effect, or tend to increase slightly, emitted particle size distribution
  - -- Have no measurable effect on trace element emissions or on trace element partitioning tendencies
  - -- Have no effect, or decrease slightly SO_3 and particulate sulfate emissions
  - -- Have little effect on total higher molecular weight organic emissions
  - -- Marginal increase in POM emissions; but the emission levels remained on the order of the detection levels of the instrument

- Emissions of the organic priority pollutants were below the detection limit for the sources tested

It must be emphasized, though, that the sources were tested only under steady operation, in short duration tests, and that the controls tested were the relatively straightforward current technology combustion modifications. Conclusions on the effects of advanced combustion modification controls, and on the potential environmental impacts of combustion sources under unsteady or transient operation must await results from the current test program.

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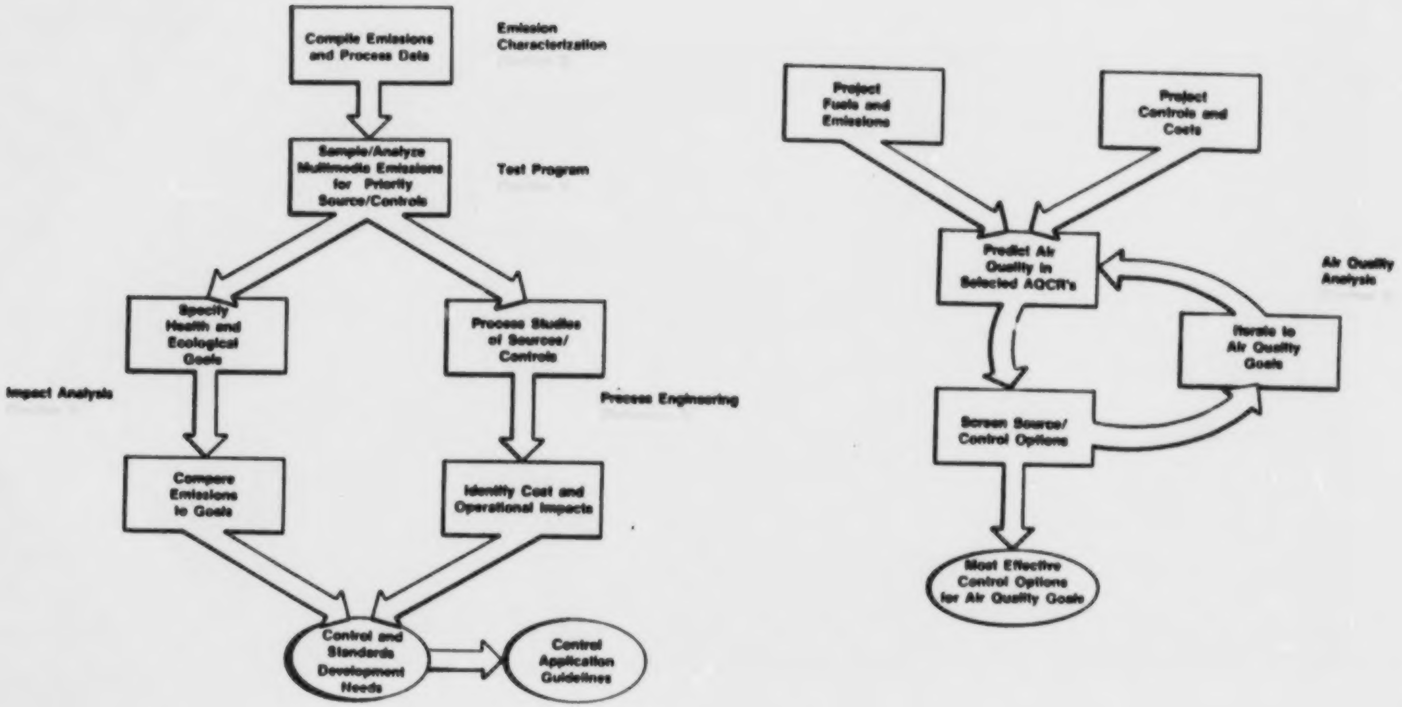
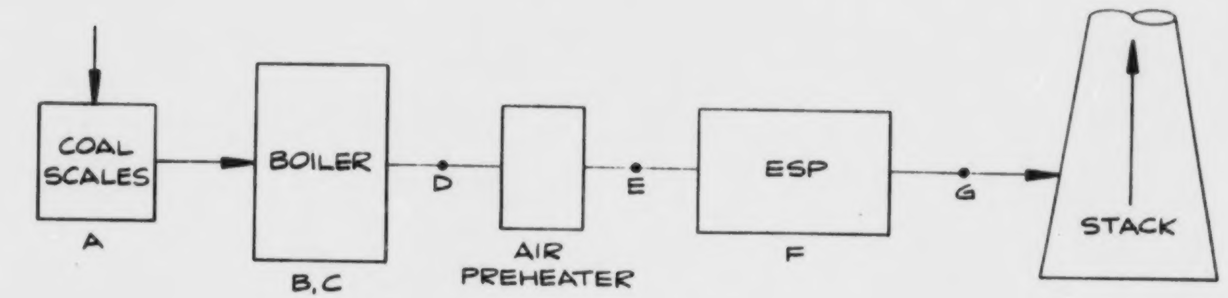

Compile Emissions and Process Data
Emission Characterization
Sample/Analyze Multimedia Emissions for Priority Source/Controls
Test Program
Specify Health and Ecological Goals
Process Studies of Sources/Controls
Impact Analysis
Process Engineering
Compare Emissions to Goals
Identify Cost and Operational Impacts
Control and Standards Development Needs
Control Application Guidelines
Project Fuels and Emissions
Project Controls and Costs
Predict Air Quality in Selected AQCR's
Air Quality Analysis
Iterate to Air Quality Goals
Screen Source/Control Options
Most Effective Control Options for Air Quality Goals

Figure 1. CMEA program approach.


COAL SCALES
A
BOILER
B, C
D
AIR PREHEATER
E
ESP
F
G
STACK

Sampling Location	Type of Sample
A -- Coal Scales	Grab Sample -- Coal
B -- Sluice Water Inlet	Grab Sample -- Sluice Water Blank
C -- Bottom Ash Outlet	Grab Sample -- Bottom Ash Slurry
D -- Airheater Inlet	Gas Sample -- Continuous Monitors
E -- ESP Inlet	Gas Sample -- SASS, EPA 5/8, Gas Grab Sample for onsite GC analysis of C_1 - C_6 HC
F -- ESP Hopper	Grab Sample -- ESP Ash
G -- ESP Outlet	Gas Sample -- SASS, EPA 5/8, Gas Grab Sample for onsite GC analysis of C_1 - C_6 HC

Figure 2. Sampling locations.

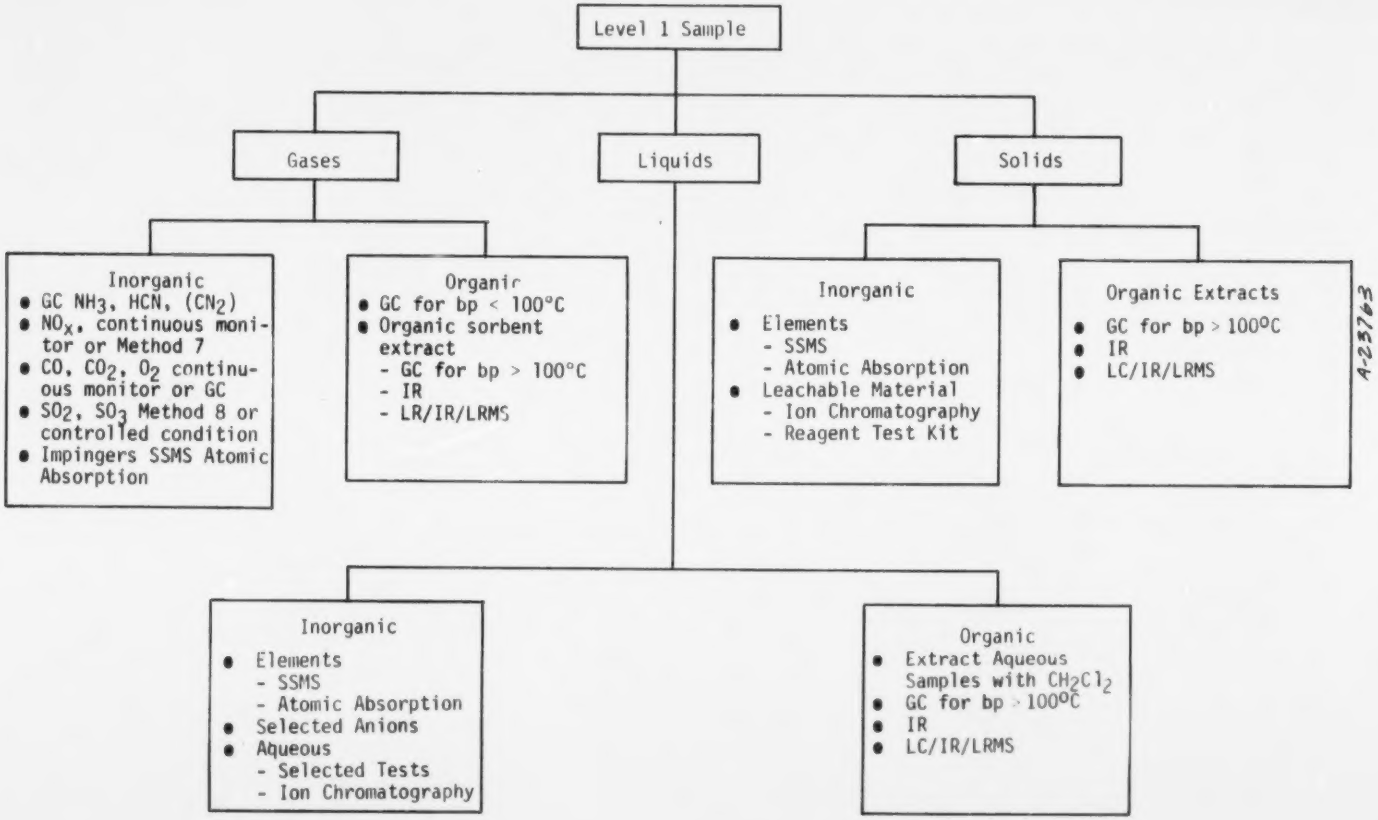

Level 1 Sample
Gases
Liquids
Solids
Inorganic
• GC NH3, HCN, (CN2)
• NOx, continuous monitor or Method 7
• CO, CO2, O2 continuous monitor or GC
• SO2, SO3 Method 8 or controlled condition
• Impingers SSMS Atomic Absorption
Organic
• GC for bp < 100°C
• Organic sorbent extract
- GC for bp > 100°C
- IR
- LR/IR/LRMS
Inorganic
• Elements
- SSMS
- Atomic Absorption
• Leachable Material
- Ion Chromatography
- Reagent Test Kit
Organic Extracts
• GC for bp > 100°C
• IR
• LC/IR/LRMS
A-23763
Inorganic
• Elements
- SSMS
- Atomic Absorption
• Selected Anions
• Aqueous
- Selected Tests
- Ion Chromatography
Organic
• Extract Aqueous Samples with CH2Cl2
• GC for bp > 100°C
• IR
• LC/IR/LRMS

Figure 3. Level 1 analysis overview.

TABLE I. CMEA FIELD TEST PROGRAM

Source Category	Description	Test Points (Unit Operation)	Sampling Protocol	Test Collaborator
Coal-fired Utility Boiler	Kingston #6; 180 MW tangential; twin furnace, 12 burners/furnace, 3 elevations; cyclone, 2 ESP's for particulate control	Baseline Biased Firing (2) BOOS (2)	Continuous NOx, SO_2, CO, CO_2, O_2 Inlet to 1st ESP: -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) Outlet of 1st ESP -- SASS -- Method 5 -- Method 8 -- Gas Grab (C_1-C_6 HC) Bottom ash Hopper ash (1st ESP, cyclone) Fuel Operating data	TVA
Coal-fired Utility Boiler	Crist #7; 500 MW opposed wall-fired; 24 burners, 3 elevations; ESP for particulate control	Baseline BOOS (2)	Continuous NO_x, CO CO_2, O_2 ESP inlet -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) ESP Outlet -- SASS -- Method 5 -- Method 8 -- Gas Grab (C_1-C_6 HC) Bottom ash ESP hopper ash Fuel Operating data Bioassay	Exxon
Oil-fired Utility Boiler	Moss Landing #6; 740 MW opposed wall-fired; 48 burners, 6 elevations	Baseline FGR FGR + OFA	Continuous NO_x, CO CO_2, O_2 -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) Fuel Operating data Bioassay	None

BOOS -- Burner out of service
FGR -- Flue gas recirculation
OFA -- Overfire air injection
LEA -- Low excess air

TABLE I. Concluded

Source Category	Description	Test Points (Unit Operation)	Sampling Protocol	Test Collaborator
Coal-fired Industrial Boiler	Traveling grate spreader stoker, 38 kg/s (300,000 lb/hr)	Baseline LEA + high OFA	Continuous NO_x, CO CO_2, O_2 Boiler exit: -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) ESP outlet -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) Bottom ash Cyclone hopper ash Fuel Operating data	KVB
Coal-fired Industrial Boiler	Traveling grate spreader stoker, 25 kg/s (200,000 lb/hr) ESP for particulate control	Baseline LEA	Continuous NO_x, CO CO_2, O_2 Boiler exit: -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) ESP Outlet -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) Bottom ash ESP hopper ash Fuel Operating data Bioassay	KVB
Oil-fired Gas turbine	T. H. Wharton Station. 60 MW GE MS 7001 C machine	Baseline maximum water injection	Continuous NO_x, CO CO_2, O_2 -- SASS -- Method 5 -- Method 8 Fuel Water Operating data Bioassay	General Electric
Oil-fired Residential Heating Unit	Blueray low NO_x furnace, Medford, New York	Continuous cycling	Continuous NO_x, CO CO_2, O_2 -- SASS -- Method 5 -- Method 8 Fuel	EPA/IERL-RTP

BOOS — Burner out of service
FGR — Flue gas recirculation
OFA — Overfire air injection
LEA — Low excess air

TABLE II. ELEMENTAL ANALYSIS: SPECIES DETERMINED

- Antimony (Sb)
- Arsenic (As)
- Barium (Ba)
- Beryllium (Be)
- Bismuth (Bi)
- Boron (B)
- Cadmium (Cd)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Manganese (Mn)
- Mercury (Hg)
- Molybdenum (Mo)
- Nickel (Ni)
- Selenium (Se)
- Tellurium (Te)
- Thallium (Tl)
- Tin (Sn)
- Titanium (Ti)
- Uranium (U)
- Vanadium (V)
- Zinc (Zn)
- Zirconium (Zr)

TABLE III. COMPOUNDS FOR WHICH GC/MS ANALYSIS WAS PERFORMED

- Acenapthene[a]
- Acenapthalene[a]
- Anthanthrene[a]
- Anthracene[a]
- Benzidine[a]
- Benzo(a)anthracene[a]
- 3,4-Benzofluoranthene[a]
- Benzo(k)fluoranthene[a]
- Benzo(g,h,i)perylene[a]
- Benzo(a)pyrene[a]
- Benzo(e)pyrene[a]
- 4-Bromophenyl phenyl ether[a]
- Butyl benzyl phthalate[a]
- Bis(2-chloroethoxy) methane[a]
- Bis(2-chloroethyl)ether[a]
- Bis(2-chloroisopropyl) ether[a]
- 2-Chloronaphthalene
- 4-Chlorophenyl phenyl ether[a]
- Chrysene[a]
- Dibenzo(a,h)anthracene[a]
- Dibenzo(c,g)carbazole[a]
- Dibenzo(a,h)pyrene[a]
- Dibenzo(a,i)pyrene[a]
- Di-n-butyl phthalate[a]
- 1,2-Dicholorobenzene[a]
- 1,3-Dichlorobenzene[a]
- 1,4-Dichlorobenzene[a]
- Bis (2-ethylhexyl) phthalate[a]
- 3,3'-Dichlorobenzidine[a]
- Diethyl phthalate[a]
- 7,12-Dimethyl benz(a)anthracene[a]
- Dimethyl phthalate[a]
- 2,4-Dinitrotoluene[a]
- 2,6-Dinitrotoluene[a]
- Di-n-octyl phthalate[a]
- 1,2-Diphenylhydrazine[a] (as azobenzene)
- Fluoranthene[a]
- Fluorene[a]
- Hexachlorobenzene[a]
- Hexachlorobutadiene[a]
- Hexachlorocyclopentadiene[a]
- Hexachloroethane[a]
- Indeno(1,2,3-c,d)pyrene[a]
- Isophorone
- 3-Methyl cholanthrene[a]
- Naphthalene[a]
- Nitrobenzene[a]
- N-nitrosodiphenylamine[a]
- N-nitrosodi-n-propylamine[a]
- Perylene[a]
- Phenanthrene[a]
- Pyrene[a]
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin
- 1,2,3-Trichlorobenzene[a]

[a] Compound in calibration standard.

TABLE IV. IONIC ANALYSIS: SPECIES DETERMINED

Chloride (Cl^-)
Fluoride (F^-)
Nitrate (NO_3^-)
Cyanide (CN^-)
Sulfate (SO_4^{2-})
Ammonia (NH_4^+)

TABLE V. BIOASSAY PROTOCOL

Sample Type	Bioassay Test Protocol	Sample Size Requirements
SASS cyclones, 10 + 3	Microbial Mutagenesis	1.0g
	Cytotoxicity, RAM	0.5g
SASS cyclones, 1 + filter	Microbial Mutagenesis	1.0g
	Cytotoxicity, RAM	0.5g
XAD-2 extract	Microbial Mutagenesis	50 mℓ
	Cytotoxicity, WI-38[a] or CHO	50 mℓ
Bottom ash	Microbial Mutagenesis	1.0g
	Cytotoxicity, RAM	0.5g
	Rodent Acute Toxicity	100 g
	Freshwater Algal Bioassay	50 kg
	Freshwater Static Bioassay	(200 ℓ if sluiced)
ESP hopper ash	Microbial Mutagenesis	1.0g
	Cytotoxicity, RAM	0.5g
	Rodent Acute Toxicity	100 g
	Freshwater Algal Bioassay	50 kg
	Freshwater Static Bioassy	

[a] WI-38 was used in the initial CMEA program

TABLE VI. BIOASSAY TESTS PERFORMED

Field Test	Bioassay						
	Sample	Microbial Mutagenesis	RAM	WI-38	RAT	Freshwater Algal	Freshwater Fish
Crist Unit 7, BOOS 2	SASS cyclones 10 + 3 m	X	X				
	SASS cyclones 1 m + filter	X	X				
	Bottom ash	X	X		X	X	X
	ESP hopper ash	X	X		X	X	X
Moss Landing Unit 6 BOOS+FGR	XAD-2 extract	X		X			
Site B Low NO_x	Bottom ash	X	X		X	X	X
	ESP hopper ash	X	X		X		
Gas Turbine Water Injection	XAD-2 extract	X		X			

BOOS2: Burner out of service test No. 2 NO_x control
FGR: Flue gas recirculation

TABLE VII. DISCHARGE SEVERITY SUMMARY FOR FLUE GAS

Component	DS Level[a]						
	Kingston Unit 6	Crist Unit 7	Moss Landing Unit 6	Site A	Site B	T.H. Wharton Unit 52	Blueray Furnace
SO_2	+++	+++	++	++	++	+	+
NO_x	+++	+++	++	++	++	+	-
CO_2	++	++	++	-	++	+	-
As	++	++	+	+	++	+	-
SO_3 (vapor)	++	++	+	++	+	+	-
CO	+	++	+	+	+	-	+
$SO_4^=$ (condensed)	++	++	+	-	-	-	-
Fe	++	++	-	+	-	-	-
Carboxylic acids	-	+	+	+	-	-	+
Be	+	+	-	+	-	-	-
Co	+	+	+	-	-	-	-
Ba	+	+	-	-	-	-	-
B	-	-	+	+	-	-	-
Ti	-	+	-	+	-	-	-
Cu	+	-	+	-	-	-	-
Cd	-	-	-	+	-	+	-
Pb	-	-	-	+	-	-	-
Cl	+	-	-	-	-	-	-
U	-	-	+	-	-	-	-

[a] Key: +++ denotes DS > 100
++ denotes DS > 10
+ denotes DS > 1
- denotes DS < 1 or species not measured

Table VIII. DISCHARGE SEVERITY SUMMARY FOR ASH STREAMS

Ash Stream	Component	DS Level[a]			
		Kingston Unit 6	Crist Unit 7	Site A	Site B
Bottom ash	Fe	-	+++	+++	++
	Mn	+	++	++	++
	Cr	+	+	-	+
	Ni	+	+	-	+
	Be	+	+	-	-
	Ba	+	-	-	-
	Tl	-	+	-	-
	Sn	-	-	+	-
Mechanical collector hopper ash	Fe	-	-[b]	++	+
	Mn	+	-	+	+
	Be	+	-	-	+
	Cr	+	-	-	+
	Ba	+	-	-	-
	Pb	-	-	-	+
	Ni	+	-	-	-
ESP hopper ash	Fe	-	+++	++	-
	Mn	+	++	++	-
	Be	+	+	-	++
	Ba	+	+	-	+
	Pb	+	+	+	-
	As	+	-	-	++
	Ni	+	+	+	-
	Cr	+	+	-	-
	$SO_4^=$	+	-	-	+
	Se	-	-	-	++
	Tl	-	+	-	-

[a] Key: +++ denotes DS > 100
++ denotes DS > 10
+ denotes DS > 1
- denotes DS < 1 or species not measured

[b] No mechanical collector at Crist Unit 7

TABLE IX. TOTAL STREAM DISCHARGE SEVERITY: SUMMARY

	Flue Gas		Bottom Ash		Hopper Ash	
	Baseline	Low NO_x	Baseline	Low NO_x	Baseline	Low NO_x
Kingston Unit 6	640	580	18	16	23	23
Crist Unit 7	740	830	160	170	150	120
Moss Landing Unit 6	160	130	a	a	a	a
Site A	150	210	120	120	110	98
Site B	170	110	b	82	45	120
T. H. Wharton Unit 52	87	52	a	a	a	a
Blueray Furnace	70[c]	25	a	a	a	a

[a] Sample no applicable to this source
[b] Sample not analyzed
[c] Baseline residential furnace evaluation based on conventional furnace data (24, 25)

TABLE X. WEIGHTED DISCHARGE SEVERITY (kg/s) -- KINGSTON UNIT 6

	Baseline	Bias	BOOS
Flue gas	4.5×10^4	3.5×10^4	3.9×10^4
Cyclone ash	19	16	16
ESP ash	6.1	6.1	5.1
Bottom ash slurry	57	53	42
Total source	4.5×10^4	3.5×10^4	3.9×10^4

Bias: biased burner firing, intermediate NO_x control
BOOS: burners out of service, low NO_x operation

210

TABLE XI. EFFECTS OF CONTROLS TESTED ON CO AND HC EMISSIONS

Test	Control[a]	CO Emissions (ppm[b])			HC Emissions (ppm[b])		
		Baseline	Intermediate NO_x	Low NO_x	Baseline	Intermediate NO_x	Low NO_x
Kingston Unit 6	Bias, BOOS	29	35	22	0	0	0
Crist Unit 7	BOOS	357	392	608	6.3	19.0	6.3
Moss Landing Unit 6	FGR, BOOS/FGR	69	10	49	0	0	0.05
Site A	OFA	243	-	483	97	-	c
Site B	LEA	65	-	36	23	-	103
T.H. Wharton Unit 52	WI	5.6[d]	-	8.1[d]	2.3[e]	-	3.5[e]
Blueray Furnace	New design	-	-	160	-	-	23

[a] Bias: Biased burner firing; BOOS: Burners out of service; FGR: Flue gas recirculation; OFA: High overfire air; LEA: Low excess air; WI: Water injection

[b] 3 percent O_2, dry

[c] Data not available

[d] 15 percent O_2, dry

[e] 15 percent O_2, wet

- Source not tested under this condition

TABLE XII. EFFECTS OF CONTROLS TESTED ON PARTICULATE EMISSIONS

Test	Control[a]	Particulate Emissions (ng/J)		
		Baseline	Intermediate NO_x	Low NO_x
Kingston Unit 6	Bias, BOOS	228	238	160
Crist Unit 7	BOOS	460	340	360
Moss Landing Unit 6	FGR, BOOS/FGR	23	22	16
Site A	OFA	13	-	24
Site B	LEA	8.0	-	10.0
T.H. Wharton Unit 52	WI	19	-	16
Blueray Furnace	New design	-	-	1.3

[a] Bias: Biased burner firing; BOOS: Burners out of service;
FGR: Flue gas recirculation; OFA: High overfire air;
LEA: Low excess air; WI: Water injection
- Source not tested under this condition

312

TABLE XIII. EFFECTS OF CONTROLS TESTED ON FLUE GAS SO_3 AND SO_4 EMISSIONS

Test	Control[a]	SO_3 Emissions (ng/J)			$SO_4^=$ Emissions (ng/J)			$\frac{SO_3 + SO_4^=}{SO_2 + SO_3 + SO_4^=}$ (%)		
		Baseline	Intermediate NO_x	Low NO_x	Baseline	Intermediate NO_x	Low NO_x	Baseline	Intermediate NO_x	Low NO_x
Kingston Unit 6	Bias, BOOS	4.3	3.9	4.5	8.6	4.4	11.0	0.85	1.24	0.98
Crist Unit 7	BOOS	9.5	4.5	3.6	11.6	9.6	8.2	0.75	0.50	0.36
Moss Landing Unit 6	FGR, BOOS/FGR	0.96	0.96	1.3	1.6	1.6	1.3	4.1	4.0	3.9
Site A	OFA	2.2	--	12.0	b	--	b	0.70[c]	--	3.0[c]
Site B	LEA	0.8	--	0.5	b	--	b	0.46[c]	--	0.46[c]
T.H. Wharton Unit 52	WI	3.0	--	5.0	4.0	--	b	9.4	--	14.3[c]
Blueray Furnace	New design	--	--	1.0	--	--	0	--	--	2.7

[a]Bias: Biased burner firing; BOOS: Burners out of service; FGR: Flue gas recirculation; OFA: High overfire air;
LEA: Low excess air, WI: Water injection

[b]Not analyzed

[c]SO_4 not included

-- Source not tested under this condition

TABLE XIV. EFFECTS OF CONTROLS TESTED ON FLUE GAS SASS ORGANIC EMISSIONS

Test	Control[a]	Organic Emissions (mg/dscm)		
		Baseline	Intermediate NO_x	Low NO_x
Kingston Unit 6	BOOS	0.124	—	0.834
Crist Unit 7	BOOS	4.23	2.320	0.722
Moss Landing Unit 6	FGR, BOOS/FGR	4.38	1.37	1.43
Site A	OFA	1.00	—	1.79
Site B	LEA	0.924	—	1.37
T.H. Wharton Unit 52	WI	1.30	—	1.10
Blueray Furnace	New design	—	—	26.3

[a] BOOS: Burners out of service; FGR: Flue gas recirculation;
OFA: High overfire air; LEA: Low excess air;
WI: Water injection
— Source not tested under this condition

214

TABLE XV. EFFECTS OF CONTROLS TESTED ON FLUE GAS POM SPECIES EMISSIONS (μg/dscm)

POM Species	Crist Unit 7			Moss Landing Unit 6			Site A		T.H. Wharton Unit 52		Blueray Furnace
	Baseline	BOOS 2	BOOS 1	Baseline	FGR	BOOS/FGR	Baseline	Low NO_x	Baseline	Water Injection	Cyclic
Chrysene/Benz (a)anthracene	—	—	0.1	—	—	0.1	--	--	--	--	—
Fluoranthene	0.1	0.1	0.2	—	0.1	0.1	--	—	--	0.5	0.03
Fluorene	—	—	0.3	—	—	0.1	--	--	--	--	—
Naphthalene	—	0.9	0.3	—	—	—	--	--	--	1.0	—
Phenanthrene/ Anthracene	0.6	1.0	0.9	0.1	0.2	0.7	—	—	0.5	1.0	0.77
Pyrene	0.1	0.3	0.3	—	—	0.2	--	--	--	0.5	0.01

BOOS: Burners out of service; FGR = flue gas recirculation
-- Compound not present or below detection level

TABLE XVI. BIOASSAY/DISCHARGE SEVERITY COMPARISON

	Bioassay Result[a]						
			Cytotoxicity				
Test/Sample	Stream DS	Microbial Mutagenesis	RAM	WI-38	Rodent Acute Toxicity	Freshwater Algae	Freshwater Fish
Crist Unit 7							
>3 μm flyash	830[b]	Neg.	ND	--	--	--	--
<3 μm flyash		Neg.	L	--	--	--	--
Bottom ash	170	Neg.	ND	--	ND	ND	ND
ESP hopper ash	115	Neg.	ND	--	ND	ND	ND
Moss Landing Unit 6							
XAD-2 extract	84	Neg.	--	M	--	--	--
Site B							
Bottom ash	82	Neg.	ND	--	ND	ND	ND
ESP hopper ash	117	Neg.	L	--	ND	--	--
Gas Turbine							
XAD-2 extract	13[b]	Neg.	--	L	--	--	--

[a] Neg: Negative, ND: Not detectable; L: Low toxicity; M: Medium toxicity

[b] Total flue gas DS cited

-- Test not conducted

TABLE XVII. COMPLETED TESTS DURING THE FIRST YEAR OF THE CURRENT PROGRAM

Source	Description	Test Points Unit Operation	Sampling Protocol	Test Collaborator
Spark ignited natural gas-fired reciprocating internal combustion engine	Large bore, 6 cylinder, opposed piston, 186.5 kW (250 Bhp)/cyl, 900 rpm Model 38TDS8-1/8	-- Baseline (pre-NSPS) — Increased air-fuel ratio aimed at meeting proposed NSPS of 700 ppm corrected to 15% O_2 and standard atmospheric conditions	Engine exhaust: — SASS — Method 5 — Gas grab (C_1-C_6 HC) — Continuous NO, NO_x, CO, CO_2, O_2, CH_4, TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries
Compression ignition diesel-fired reciprocating internal combustion engine	Large bore, 6 cyclinder opposed piston, 261.1 kW (350 Bhp)/cyl, 900 rpm Model 38TDD8-1/8	-- Baseline (pre-NSPS) — Fuel injection retard aimed at meeting proposed NSPS of 600 ppm corrected to 15% O_2 and standard atmospheric conditions	Engine exhaust: — SASS — Method 8 — Method 5 — Gas grab (C_1-C_6 HC) — Continuous NO, NO_x, CO, CO_2, O_2, TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries
Low NO_x residential condensing heating system furnished by Karlson's Blueburner Systems, Ltd. of Canada	Residential hot water heater equipped with M.A.N. low NO_x burner 0.55 ml/s (0.5 gph) firing capacity; Condensing flue gas	Low NO_x burner design by M.A.N.	Furnace exhaust: — SASS — Method 8 — Method 5 — Gas grab (C_1-C_6 HC) — Continuous NO, NO_x, CO, CO_2, O_2, TUHC Fuel Waste water	New test
Rocketdyne/EPA Low NO_x residential forced warm air furnace	Residential warm air furnace with modified high pressure burner and firebox. 0.83 ml/s (0.75 gph) firing capacity	Low NO_x burner design and integrated furnace system	Furnace exhaust: — SASS — Method 8 — Controlled condensation — Method 5 — Gas grab (C_1-C_6 HC) — Continuous NO, NO_x, CO, CO_2, O_2, TUHC Fuel	New test

UTILITY BOILER ENVIRONMENTAL ASSESSMENT -- THE EPRI APPROACH

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ABSTRACT

EPRI's environmental assessment program for air emissions comprises physical and chemical characterization, ecological and human health research and an integrated analysis of costs, benefits and risks associated with various generating technology and emission control approaches. Physical and chemical characterization is approached from both a regional and localized aspect and includes primary and secondary pollutants. Regional transport research began with the Sulfate Regional Experiment (SURE) in the Northeastern U.S. and continues with visibility and acid deposition research in the East and West.

Localized plume distribution is being studied on a site-specific basis beginning with simple and continuing with more complex terrain. Both efforts include extensive field measurement programs designed to evaluate or develop modeling techniques for predicting utility contributions to ground-level concentrations or deposition.

Ecological research currently emphasizes the potential effects of acid deposition and includes watershed, aquatic, forest, crop, and grassland research. Current studies focus on biogeochemical processes which influence resultant soil and water acidity and nutrient balance.

Health effects research concentrates on determining human health effects of airborne utility emissions using animal studies, human clinical studies and epidemiology.

The ultimate objective of these research efforts is the evaluation of relative risk of generation mixes and emission control strategies.

UTILITY BOILER ENVIRONMENTAL ASSESSMENT - THE EPRI APPROACH

INTRODUCTION

The purpose of my presentation is to describe NO_x research results, research in progress and research planned by the Environmental Assessment Department of EPRI.

The Environmental Assessment Department is part of the Energy Analysis and Environment Division, one of six technical divisions at EPRI.

The primary objectives of the EAD are to identify, measure and determine the relative importance of emissions from electricity generation transmission and use. The Department comprises four program areas: Environmental Physics and Chemistry, Ecological Studies, Environmental and Occupational Health, and Environmental Risk and Issues Analysis. The research I will discuss today is planned and executed under the auspices of one or more of these programs. It is apparent that we are organized along disciplinary lines, and you will see from my discussion that research projects tend to fall within one of these four categories.

My objectives in this presentation are:

1) to illustrate through examples of research results, research in progress and research planned what we see as the most important areas of study with reference to NO_x,

2) to open our research program to investigators involved in similar or allied pursuits in hopes of encouraging an exchange among our staffs, and

3) to invite your comments on the directions we have established and the questions we are asking through research.

My presentation is divided into six major areas: NO_x emissions, transformation and transport, human health effects, ecological effects, materials damage and visibility degradation (see Figure 1). Discussion under each of these headings will be organized, with minor variations, as follows: results to date, research in progress, and planned research.

NO_X EMISSIONS

Results to Date

Our first NO_x emissions project began in 1975 prompted by published reports of elevated ozone concentrations in power plant plumes. The objectives of this initial research were to determine whether ozone was generated in power plant plumes and to develop a qualitative understanding of dominant influences on the potential for such ozone generation. Investigative methodology included reactive plume modeling and measurements of plumes at four southwestern and western power plants representing gas- and coal-fired boilers in dry or humid climates (1,2,3).

Subsequently, interest turned to the potential of NO_x to contribute to the formation of NO_2 and nitrates on a regional scale. This regional research will be discussed under transformation and transport.

The next area of interest was the formation of nitrates and nitric acid as potential contributors to visibility degradation and acidic precipitation. A modeling approach was obviously required to evaluate the impact of an individual or group of power plants on air quality at some distance from the source. In order to accurately model NO_x reactions, we needed to develop an understanding of key reactions and reaction rates. Chamber research was begun in 1978 in this pursuit and continues to date.

Plume measurements have shown ozone formation in the West and Southwest under the conditions studied to be a rare occurrence. The chamber studies indicated that oxidation of NO_x to HNO_3 and NO_3 in gas phase reactions depends on the presence of hydrocarbons.

On-going Research

Current research related to NO_x emissions includes validation of the chamber studies by aircraft sampling in a power plant plume and a more general plume model validation project (4). In this project, oxides of nitrogen are of major importance. Ground level pollutant characteristics predicted by plume models are being investigated in addition to chemical and physical transformations which will require validation of reactive plume models. We plan eventually to include a moderately complex and a complex site in addition to these current studies at a flat terrain site.

TRANSFORMATION & TRANSPORT

Results to Date

As mentioned above, EPRI's attention turned early to regional considerations with the Sulfate Regional Experiment (SURE). I have nothing to report now on results because final reports are in preparation. However, I will summarize the objectives and approach of the SURE (5).

SURE began in 1977 with the primary objective of defining the relationship between emitted primary pollutants (e.g., SO_2) and regional, ambient concentrations of secondary pollutants (e.g., sulfates). Subobjectives included:

- the establishment of a regional air quality data base through measurements made at ground level and aloft, and
- the determination of the location and magnitude of emissions during air quality measurement periods.

It was hoped that with this approach it would be possible to derive quantitative methodology for relating emissions from power plants to regional air quality as measured by SO_2 and particulate sulfate. In addition to measuring SO_2 and sulfates, nine ground-based stations measured continuously for nineteen months NO/NO_x, O_3, temperature, dewpoint and suspended particles. Aircraft which operated six days during the central month during each season (seven "intensives" during the nineteen month field program) measured SO_2, O_3,

NO/NO_x, b_{scat} and condensation nuclei. SURE field sampling is now complete and the final report is being written.

In early 1978, the SURE program was supplemented with a precipitation chemistry component consisting of nine stations sited in close proximity to the nine SURE continuous monitors. The primary objective of this research was to relate rain pH to air quality or emission parameters already included in the SURE.

Also in 1978, outdoor air quality studies were supplemented with characterization of the indoor environment as a function of outdoor pollution levels, structure type, geographic locality and other variables including presence of smokers and type of heating and cooking fuel (6).

Planned Research

We are currently in a major planning exercise regarding regional air quality studies. This process consists of a "Delphi-type" survey of industry representatives, academicians and agency personnel which asks for a ranking of research areas, forcing functions and research aspects. SO_x and NO_x rank high in importance and have been combined for planning purposes. The primary forcing functions or motivating factors for research are the potential for oxides of nitrogen to contribute to human health, ecological or esthetic effects and materials damage. The most important research aspects are chemical transformation, regional transport, wet and dry deposition, synthesizing models and atmospheric dilution.

A workshop was held in April 1978 to review effects of trace nitrogen compounds on human health and welfare, identify mechanisms of nitrogen compound formation and transport, assess the present state of knowledge of these phenomena and recommend and prioritize critical areas of research (7). Participants agreed research was needed in all aspects and most importantly in removal (from atmosphere) mechanisms, transformation in plumes and ammonia flux.

HUMAN HEALTH EFFECTS

Identified Research Needs

A planning study accomplished in 1978 (8) evaluated existing information on the health effects of nitrogen oxides, identified the need for better methodology and the existence of gaps in knowledge and recommended a research program appropriate for EPRI and responsive to the need for information. At the top of the list of needed research was the development of more precise and accurate methods for monitoring NO_2/NO_3^-, peroxacyl nitrates (PAN) and N-nitrosamines. Additional research needs include:

- characterization of NO_2/NO_3^- in respirable suspended particles,
- animal inhalation toxicology of
  - NO_2/NO_3^- aerosols
  - N-nitrosamines
  - PAN
- human clinical studies for threshold limit values and respiratory function response for
  - PAN
  - NO_2/NO_3^- aerosols, and
- human epidemiology for
  - NO/NO_2
  - NO_2/NO_3^-
  - PAN
  - N-nitrosamines.

Results to Date

In response to the need for better monitoring methodology, research was begun to determine the rates and amounts of artifact nitrate formation on standard fiberglass filter media; to devise, if possible, correction factors which might be applied to historical nitrate concentrations; to test other media; and, to recommend best available sampling and analysis techniques.

The research clearly demonstrated large and erratic artifact formation on untreated glass fiber filters (9). Anywhere from 10 to 100 percent of the reported nitrate was attributed to on-filter reactions, with a most likely value of about 20 percent. Unfortunately, it is not likely that historical records can be corrected because although artifact formation varied according to experimental conditions, it also varied strongly and in an unpredictable way on the filter handling procedures used prior to exposure.

Most health-related NO_x research is still underway, so results are limited but do not indicate that exposure to ambient outdoor levels of NO_2 and nitrate is harmful to health. There is some evidence that elevated NO_2 indoors may be linked to increased respiratory disease in children.

On-going Research

Current research in animal inhalation toxicology involves an increased range and duration of exposure concentrations and interactions of NO_2 with SO_2, O_3 and SO_2 and O_3 together.

Planned Research

The five-year plan includes animal inhalation toxicology studies of chronic and acute exposures to mixed gases, human clinical studies of acute effects of NO_2 alone and epidemiological studies of chronic effects of indoor and outdoor exposures to ambient concentrations.

ECOLOGICAL STUDIES

Results to Date

EPRI's ecological research on effects of oxides of nitrogen focuses primarily on the contribution of nitrate through dry and wet deposition. The majority of research underway in this area has begun recently. One study from which there are interim results is the Integrated Lake/Watershed Study (ILWAS) which is being conducted at three Adirondack (New York) Lakes. In this project, water chemistry is determined from the incoming rainfall above the canopy and as the water passes through the watershed/lake system.

Rainfall chemistry analysis has shown:

- NO_3^- to vary less than sulfate over the year,

- o NO_3^- concentration is about one-fourth that of $SO_4^=$ in the summer and about equal in winter, and
- o a relatively low $SO_4^=/NO_3^-$ ratio for snow when compared to rain.

On-going Studies

The field program for the Integrated Lake/Watershed study is scheduled to end in December 1981 and will be followed by a year of data analysis and model development and refinement. An interim report will be published in the fall of 1980.

Other on-going research falls under four categories: forests and surface waters, agricultural crops, aquatic biota and economic assessment. Current research in forests is focused on a microcosm approach to identifying key parameters in forests sensitive to acidic precipitation.

Research on effects on agricultural crops and aquatic biota has only recently begun. Crop research consists primarily of experimental field studies with some use of laboratory microcosms. In aquatic studies, research will focus on the effects of acidification and potentially resultant toxic metal concentrations on decomposition processes.

Planned Research

Future research in the lake/watershed approach will focus on application and validation (and additional development, if necessary) of the ILWAS model using watersheds located in other geographic locations and exhibiting other geological, climatological and biotic regimes.

In forest studies, it is hoped that expansion of microcosm research to field studies will increase our understanding of acidification processes and forest ecosystem responses.

Interest in grasslands is fostered primarily by concern about possible effects of sulfur deposition, primarily in the form of SO_2. Although NO_2 is not considered a regional problem, the deposition of secondary products, nitrates, must be considered in the overall investigation of the impact of power plant emissions. The approach will be to look at nutrient cycling, yield and productivity.

EPRI's crop effects research will focus on acid rain rather than gaseous pollutants as has most previous research. Emphasis will be on ecological processes leading to changes in fertility, yield and quality of agricultural soils and plant species. The ultimate objective is to develop mitigation and management methodology where the need is shown by research.

For aquatic systems, the on-going research on effects of acidification of decomposition mentioned above will be expanded to include effects on other processes hopefully leading to predictive capability and results which will refine some aspects of the lake/watershed modeling. Studies of effects on specific species or communities will be carefully chosen to complement research being conducted by EPA, universities and federal and state resource management agencies. Mitigative strategies (e.g., liming and fertilization) will be investigated.

MATERIALS DAMAGE

The approach to date has been to refine damage estimates for various surfaces and their distribution throughout the U.S. The primary pollutant of interest has been SO_2 rather than NO_x. Urban Boston was used as a prototypical site. Results should be published within the next year. Currently, no additional work is underway. In the future, such estimates would be used in overall risk/cost/benefit analyses of alternative generation and emission control technologies.

VISIBILITY

On-going Research

EPRI's visibility research has taken three fundamental approaches:

- development and intercomparison of quantitative instrumental methods for measuring visibility
- development of regional data bases on visibility variability, causes of visibility impairment, and the development of reliable regional visibility models, and
- the assessment of social and economic costs generated by visibility impairment and the remedial costs at various levels of protection.

EPRI's first step was to establish one visibility station in the Southwest and one in the Northeast to serve the first purpose mentioned above, i.e., methodology intercomparison and, through fine particle measurements, begin building a base of information for understanding the relationship between ambient air quality and visibility.

Following these initial tests, additional measurement stations were established (two in the Northeast and five in the Southwest) to acquire accurate and reliable information on the regional distribution and variability of visibility impairment.

Concurrently, EPRI has funded the development and testing of an automated multi-wavelength telephotometer which is now in the field testing stage (10).

The third fundamental approach mentioned above was the development of social and economic benefit/cost comparisons. Among the important objectives are:

- evaluation and development of methodology for estimating air pollution damage
- determination of the degree to which anthropogenic sources, particularly power plants, are associated with visibility impairment
- estimation of costs associated with reducing power plant emissions, and
- identifying and quantifying economic and social benefits from improved visibility.

Planned Research

EPRI plans to expand the Western visibility network during 1981. Data from these regional networks will provide data initially for setting baselines and for empirical studies of the causes of visibility impairment. Eventually, such data will be used in the development of regional models which could be used to examine the potential for specific sources to impact visibility in defined geographic areas.

Social and economic assessments will hopefully lead to a better understanding of source relationships, social costs and benefits of visibility impairment and improvement and the impact of emission controls on visibility in specific geographic areas.

SUMMARY

I have discussed the EPRI Environmental Assessment Department's program of NO_x research. This program includes six major areas: NO_x emissions, transformation and transport, human health effects, ecological effects, materials damage and visibility degradation. My primary objective was to open channels of exchange between our staff and contractors and other researchers doing similar or complementary research. We believe it is very important to coordinate such research activities to best utilize limited resources whatever their source. We invite your comments and contacts and hope that you might share with us your results, current research and plans for the future.

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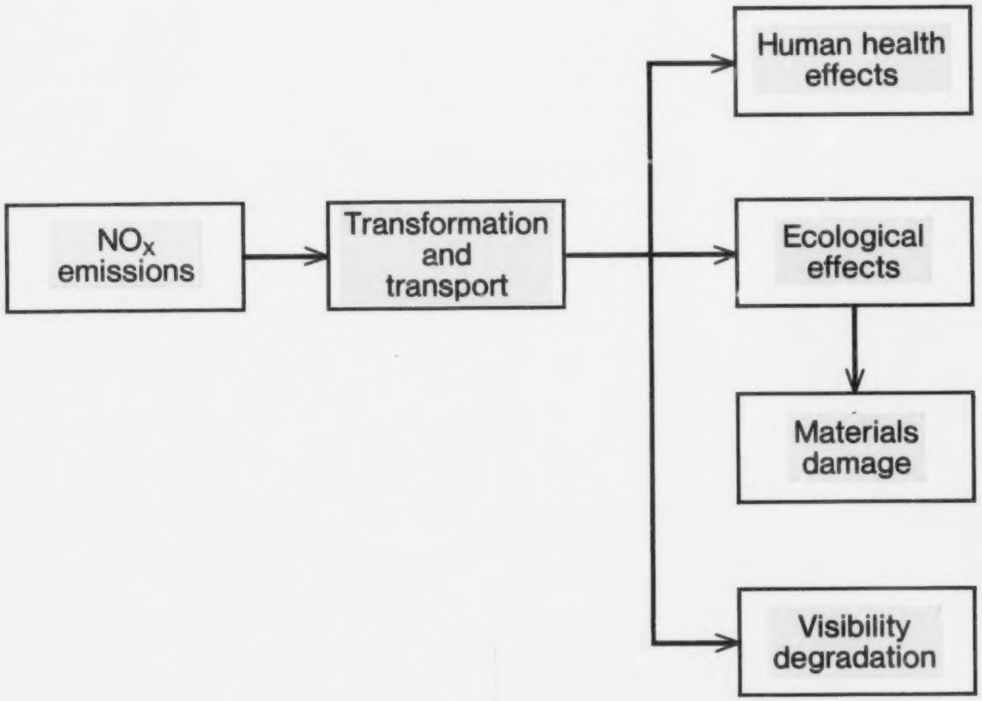
NO_x emissions
Transformation and transport
Human health effects
Ecological effects
Materials damage
Visibility degradation

Figure 1. NO_x Major Issues

CHARACTERIZATION AND OXIDATION OF DIESEL PARTICULATE

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ABSTRACT

This study is being conducted for the Environmental Protection Agency to evaluate emissions control on light-duty diesel vehicles by postcylinder oxidation. The primary objective is to determine the feasibility of thermal or catalytic oxidation as a means of diesel particulate emissions control.

The program plan includes a review of the state of technology, detailed chemical and physical characterization of the particulate from a light-duty diesel engine, bench experiments to define the ignition and oxidation properties of the particulate, experiments with catalytic ignition of particulates, and experimental evaluation of concepts and devices for particulate emission control by oxidation in the exhaust of an engine.

The particulate characterization is being carried out using an Oldsmobile 4.3-liter diesel engine coupled to a dynamometer with direct and diluted exhaust particulate sampling and measurement. Bench experiments are being conducted with various types of hot-tube reactors and instrumentation.

The particulate characteristics being measured include: mass concentration; soluble organic content; carbon, hydrogen, and ash; trace mineral content; surface area; size distribution; and volume concentration. Results to date show that: as engine load is increased mass concentration increases substantially and soluble organic content decreases, both hydrogen content and ash content vary between 1/2 and 2 percent, the surface area is approximately 100 m^2/g, and the mass median particle diameter increases with load increase and is in the range of 0.1 to 0.3 μm.

Preliminary catalytic ignition results indicate that the ignition temperature of the particulate can be substantially reduced (at least 150 C) by application of small concentrations of metal salt solutions. In addition, it has been found that the catalytic action of the metal salt is enhanced by admixing salts such as sodium or ammonium chloride and nitrate. Copper salts have been found to work best of the materials studied to date.

ACKNOWLEDGMENTS

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SECTION 1

INTRODUCTION

Diesel engines are becoming available in increasing numbers in passenger car service because of their good fuel economy in comparison to conventional gasoline engines. Though the diesel exhaust is relatively clean with respect to unburned hydrocarbons and carbon monoxide, it contains particulate emissions that are 30 to 50 times greater than those produced by the catalyst-equipped gasoline engine. These diesel particulate emissions not only will contribute to already high levels of total suspended particulate (TSP) in urban areas, but certain components of the particulates have been identified as carcinogenic, thereby creating a potentially greater health hazard.

The U.S. Environmental Protection Agency (EPA) has established regulations on the amount of particulate that may be emitted by each light-duty diesel vehicle. These standards, based on the presently used Federal Test Procedure (FTP) with a particulate measurement procedure added, are 0.6 grams per mile (0.37 g/km) for 1982 model year vehicles and 0.2 grams per mile (0.12 g/km) for 1985 model year vehicles. These emission levels are based on the need to reduce (or prevent an increase in) the total suspended particulate (TSP) levels in urban areas as diesels become more numerous. It is quite possible that even more stringent particulate emission standards will have to be set in the future to control the toxicity problem.

For these reasons, the EPA is interested in the state of technology of diesel particulate emission control, and in particular, in the feasibility of controlling the particulate emissions by afterburner techniques. A program was already under way at Battelle's Columbus Laboratories to assess the performance of industrial afterburner emission control devices, hence, it was a logical extension of that program to include diesel particulate emission control by afterburners.

The objective of the diesel afterburner study is to evaluate emissions control on light-duty diesel vehicles by postcylinder oxidation. Because of the special nature of the diesel emissions problem, we have defined the scope of the program as a study of the ignition and oxidation characteristics and requirements of diesel exhaust particulates.

SECTION 2

PROGRAM PLAN

This study comprises a review of the state of technology, detailed chemical and physical characterization of the particulate from a light-duty diesel engine, bench experiments to define the ignition and oxidation properties of diesel particulate, experiments with catalytic ignition of particulates, and experimental evaluation of concepts and devices for particulate emission control by oxidation in the exhaust of an engine.

STATE-OF-TECHNOLOGY REVIEW

The state-of-technology review is directed towards determining the current understanding of the nature of the diesel particulate primarily with respect to its ignition and burning characteristics, and assessing the current status of development of particulate emission control by oxidation. It was hoped that specific devices or concepts would be found in the course of this review that could be evaluated in the program. However, industry sources were not encouraging in having devices or concepts sufficiently developed for evaluation at this time.

A report on the technology of thermal and catalytic oxidation of diesel particulate was published in October, 1979.(1)

CHEMICAL AND PHYSICAL CHARACTERIZATION

This task of the program is aimed at determining the chemical and physical nature of the diesel particulate and the exhaust environment as they relate to the requirements for thermal or catalytic oxidation of the particulate. The information developed in this task is being used both in the evaluation of current prototype technology and in the development of particulate oxidation principles and methodologies. Particulate characteristics of special interest include surface area, ash chemistry, size distribution, trace mineral content, total mass concentration, and soluble organic content.

PARTICULATE IGNITION AND OXIDATION PROPERTIES

In this task, experiments are being conducted to study the ignition and burning characteristics of diesel particulate. These experimental results will establish a basis for developing particulate oxidation concepts and for evaluating available prototypes. The specific objectives include determining (1) how readily the particulate ignites, (2) how rapidly it burns, (3) whether the behavior can be modified, and (4) what the products of combustion are.

The bench experiments on ignition and oxidation properties are under way but currently available results are too preliminary to report at this time.

CATALYTIC IGNITION OF PARTICULATE

The primary activity in this task is an investigation of the catalytic approach to particulate oxidation. The feasibility of using inorganic salts, metal oxides, or other materials to promote the ignition and oxidation of the particulate is being studied in bench experiments involving a hot tube reactor. The experiments are being conducted to identify potentially catalytic materials, to explore methods of catalyst application, and to determine the magnitude of the catalytic effect and the catalytic material amounts required to achieve that effect.

In this task and in the task on particulate ignition and oxidation properties, we are also seeking to determine if a relationship exists between the chemical and physical characteristics of the particulate and its oxidation properties. Knowledge of such a relationship may contribute to the development of a successful oxidation-type particulate control system.

EVALUATION OF CONCEPTS AND DEVICES

The objective of this task is to evaluate on the engine any promising concepts or devices for particulate control by oxidation which result from the state-of-technology review or from the bench experiments.

SECTION 3

EXPERIMENTAL RESULTS

PARTICULATE CHARACTERIZATION

Description of Experimental Facility

Figure 1 is a schematic drawing of the experimental facility being used in this program. The engine is a 4.3-liter General Motors passenger-car diesel and is coupled to a 175-hp eddy-current dynamometer. The exhaust system consists of standard vehicle exhaust pipe, muffler, and tailpipe components. A dilution tunnel-CVS system combination is used consistent with present practice for collecting and studying diesel exhaust particulates. The 560-mm diameter by 5.5-meter long stainless steel dilution tunnel is installed between the CVS system and its filter assembly.

Instrumentation includes gas analyzers for exhaust emissions measurement, thermocouples for engine, exhaust, and dilution system temperature measurement, stack sampling systems for particulate collection on filters, and an Electrical Aerosol Analyzer and a Laser Light-Scattering system for particle size distribution and volume concentration measurements.

The particulate characteristics are being studied primarily by means of a dilution system. As will be brought out later in this section, there are limitations to the validity of this approach. However, the dilution system does provide a controllable means for particulate collection and measurement and has been established as the accepted method for determining particulate emission rates, therefore, this approach serves a useful purpose. Particulates are also being collected directly from the exhaust system for use in the bench experiments and for characterization.

Engine Baseline Operation

Before particulate characterization experiments were begun the engine was operated at various speed/load conditions to establish its baseline operating characteristics. In one series of test runs the engine was operated at wide open throttle over a speed range from 800 to 3200 rpm. The resulting engine performance data were compared with representative performance data obtained from Oldsmobile Division of General Motors.(2) The test engine performance data were close to the representative engine data except for air-fuel ratio. The test engine operated approximately 1 to 2 air-fuel ratio numbers richer than the "representative" data. Richer operation will, in most cases, yield higher particulate emissions, which, for the purposes of this program is not an undesirable characteristic.

For another series of baseline tests, a number of engine speed/load conditions were selected to represent typical vehicle road-load operation. Nine modes were selected representing 25 mph, 35 mph, and 55 mph at light, medium, and heavy loads. These modes were run and the data are summarized in Table I.

Particulate Characterization Methods

Particulate characteristics which have been measured in this program are:

- Mass concentration
- Soluble organic content
- Carbon, hydrogen, and ash
- Trace mineral content
- Surface area
- Size distribution
- Volume concentration.

Mass concentration of the particulate is determined by weighing the particulate collected on a 100-mm diameter Teflon-impregnated glass fiber filter sampling from the dilution tunnel using conventional EPA Method 5 stack sampling systems. These sampling systems consist of a vacuum pump, a dry-gas meter, a flow-indicating orifice, a condenser train, a flow control valve, and appropriate thermocouples and manometers. Sampling time, sampling rate, and sample temperature can be varied over reasonable ranges as desired. Concentration of the particulate in the exhaust system is calculated from the dilution tunnel data using the dilution ratio which is determined from CO_2 measurements made in the exhaust gas, dilution air, and dilution tunnel.

The soluble organic content of the collected particulate is determined by solvent extraction. In this extraction process, soluble organic material is removed from the filter (or from loose particulate) by Soxhlet extraction using toluene as the solvent. The extraction is carried out for 32 to 48 hours at a 10-minute cycle rate. After extraction the solvent is concentrated by rotary film evaporation and a known fraction removed for gravimetric analysis.

The carbon and hydrogen measurements are made using a Perkin-Elmer Elemental Analyzer. The ash was determined by weighing the sample before and after oxidizing it in a muffle furnace.

The trace mineral content is determined by spark source mass spectrograph.

Surface area is measured by the BET procedure.

Size distribution and number and volume concentration measurements are made by Electrical Aerosol Analyzer and Laser Light-Scattering instruments.

Characterization Results

A major thrust of the particulate characterization experiments has been to determine if the engine operating conditions alter the chemical or physical nature of the particulate in a manner that might be taken advantage of in devising an oxidation technique. Thus, a number of engine tests were run using the operating modes shown in Table I. It was noted early in the experimental work that the total mass concentration and the soluble organic content of the particulate were significantly affected by engine load and speed. To define more completely these influences, additional load conditions were run at each engine speed.

Figure 2 shows the effect of engine speed and load on particulate mass concentration. The particulate concentration is plotted against exhaust temperature rather than horsepower because it is believed that temperature bears a more direct relationship to particulate formation. The trend of increasing particulate concentration with increasing load has been observed by others.(3) It is interesting to note that as load (temperature) is increased, specific fuel consumption decreases (see Table I), meaning the fuel is burned more completely, but the particulate concentration increases sharply.

Figure 3 shows the effect of engine speed and load on the particulate soluble organic content. As with the particulate mass, the soluble organic content is plotted against exhaust temperature rather than engine horsepower. Engine speed does not seem to have as significant an influence on the soluble organic content as it does on the mass concentration. As one might expect if condensation plays a substantial role in the association of the organic material with the particulate, the soluble organic fraction decreases significantly as exhaust temperature is increased by increasing load.

In the course of collecting data to determine the trends shown in Figures 2 and 3, we noted that the soluble organic content measurements were sensitive to certain parameters of the dilution and sampling procedure. An investigation was carried out to determine the specific effects of sampling rate, sampling time, sample temperature, and dilution ratio on the soluble organic content measurement.

Figures 4, 5, and 6 show some of the results of this investigation. Figure 4 shows the effect of sampling rate on soluble organic fraction; Figure 5 shows the effect of sample temperature; and Figure 6 shows the effect of sampling time. The sample temperature effect is similar to that which has been noted by General Motors researchers.(4) The dilution ratio test results were not consistent enough to indicate a trend.

The conclusion to be drawn from these data is that artifacts are being created in the sampling process. It would require considerably more investigation than is warranted in this program to establish the nature and magnitude of the artifact or artifacts. Fortunately, the sampling process effects that are seen in Figures 4, 5, and 6 do not appear to alter significantly the qualitative relationships between soluble organic content and engine speed and load. In this program it is more important to determine if differences exist due to engine operating mode differences than it is to determine precise values for key particulate characteristics. Furthermore, we must also establish whether these differences which do appear to exist result in differences in the ignition and combustion characteristics which are being studied in the bench experiments.

Loose particulate samples are also being collected from the engine exhaust system, both to provide larger amounts of particulate for the bench experiments and to characterize the particulate as it exists in the exhaust pipe before passing through the muffler and tailpipe and into the dilution tunnel. The present method being used to collect this loose particulate is to brush it out of the exhaust pipe with a nylon brush assembly made to fit the pipe inside diameter. The procedure has been to clean the 7-foot exhaust pipe section before a test run, and then to allow the particulate to collect on the surfaces during a period of 6 to 7 hours or for the duration of a day's testing. The deposited particulate is then brushed into a glass container which is sealed from air and light.

This procedure was followed for a number of test runs including both single speed/load runs and runs where either the speed or the load or both were varied during the test period. Table II summarizes characterization data obtained on these loose particulate samples. Several of the samples are being used in the bench experiments. One noteworthy characteristic of these samples is that in most cases the soluble organic content is substantially lower than in filter samples collected from the dilution tunnel under the same or similar engine operating conditions as shown in Column 8 of Table II. We theorize that this is due to the organic material continuing to associate with the particulate throughout the exhaust system and possibly even into the dilution system. However, it is also possible that the particulate deposited on the exhaust pipe walls will lose some organic material as it continues to be exposed to the hot exhaust gases.

Table III presents the results of the trace element analysis performed on two loose particulate samples by spark source spectrograph.

The major elements appear to be carbon, iron, sulfur, phosphorus, calcium, silicon, and zinc. The two samples represent widely different engine operating conditions and substantial differences in some of the constituent elements are noted. Further trace element analyses may be performed if the bench experiment results indicate a need for such data.

Only one surface area measurement has been made at this time. The resulting value, by the BET procedure, was approximately 100 m^2/g, which appears to agree with published data.(5)

The size distribution measurements by Electrical Aerosol Analyzer showed a shift in the mass median diameter as engine load was changed. Figure 7 shows this shift. As engine load (represented by exhaust temperature) is increased at constant speed, the mass median diameter increased also. This phenomenon indicates agglomeration is occurring with increasing load which could help to explain the mass concentration increase with load increase. Particles too small to be captured on a filter at lower loads agglomerate to larger particles as load increases thereby increasing the filter-collected mass. Others have also observed this effect.(6) Figure 7 also shows that higher speed operation results in smaller mass median diameter, a phenomenon probably related to residence time. i.e., less time available for agglomeration at higher engine speeds.

The Laser Light-Scattering instrument is intended to be used in this program to provide an instantaneous measure of particulate mass concentration in the dilution tunnel. When concepts or devices for particulate control by oxidation are being evaluated on the engine, there may be transient effects on the particulate which could not be detected by the filter-collection method.

In the preliminary evaluation of the Laser-Light Scattering instrument, data were obtained by both filter collection and light scattering with the engine operating at constant speed and different loads. Figure 8 shows the results of this experiment. The light-scattering data are seen to follow the filter data fairly closely.

CATALYTIC IGNITION

Background and Experimental Approach

A basic problem with the particulate when entrained in the diesel exhaust is that it is too dilute to burn. This can be remedied by collecting the material on a filter or trap. In this concentrated form the average heat loss is reduced and conditions for combustion are more favorable.

There are a number of design concepts for trapping and oxidizing the particulate emissions from diesel engine operation. Although the requirements for successful application of each of these concepts can be described qualitatively, neither the character of the particulate, the service requirements, nor the limitations imposed by automobile application are well enough described to permit firm choice among these concepts or the complete rejection of any. In this study it is assumed that the particulate has been trapped in a fashion suitable to the catalysis demonstrated here.

In the present work, the opportunities for catalytic promotion of ignition are being surveyed by using catalytic salts that are deposited directly on previously trapped particulate. In principle this would be done directly in the exhaust system of the automobile, in the bench experiments we have removed the collected particulate from the exhaust system, catalyzed it, and examined its ignition properties in a separate system. Lowered ignition temperatures achieved in this way facilitate the onset of combustion which, because of its highly exothermic nature, produces a large local increase in temperature at which the sample is rapidly burned.

With suitable sample geometry, only the ignition need be catalytic and this is the effect being monitored here. The situation for achieving ignition in some volume element of a reactor can be described with the help of the theory employed by Wagner(7) and Frank-Kamenetskii(8). Usually the ignition temperature lies well above the temperature at which the first significant heat effect due to oxidation is detected, and at ignition the excess heat generated over that lost by the volume element causes that element to suddenly rise in temperature well above the environment temperature. In so doing it passes from activity limited oxidation to transport limited conditions and usually exceeds the kinetics that can be expected for the catalytic surface reaction processes.

The only form of catalysis that has been described in any detail for oxidation of carbon particulate is that developed years ago for removal of soot accumulation from flues and furnaces by the use of inorganic salts deposited on the carbon particle. The U.S. Bureau of Mines Bulletin 360(9) provides an understanding of the level of development of this form of carbon particulate oxidation catalysis. More recently(10) salt additives were studied as catalysts for the oxidation of high purity graphites.

It is of interest to note that English patents for inorganic soot removers began to appear in 1856 covering the use of ordinary alkalis or salts such as sodium chloride, quicklime plus soda ash, magnesia, copper salts, and others. American patents started in 1892 covering similar compounds and especially chlorides of a number of elements such as zinc. From the earliest patents the use of chlorides has been favored for such purposes. Bulletin 360 of the U.S. Bureau of Mines(9) lists 59 compositions tried by them and exhibiting decreases in ignition temperatures of as much as 287 C. By this means the ignition temperature was lowered from 613 C to a minimum of 326 C in normal air.

In all of these tests the volatility of the salt used was an important characteristic. Initially, the salt was applied by vaporizing it and allowing it to deposit onto soot that had been accumulated previously on a test screen. The action by which the salt catalyzed burning was not specified, but some relatively contemporary publications suggest mechanisms that do not seem to have been further investigated.

For instance, Cassel(11) noted that soot deposited on the etched or ground surfaces of Jena glass ignited much more easily and burned more rapidly than soot on adjacent smooth surfaces of the glass. From evidence for oriented crystal growth of soot particles on surfaces he suggested that the ground surfaces interrupted crystal growth during soot deposition because of surface irregularity and also helped to prevent secondary crystal growth during oxidation (burning). He reasoned that the salt deposits condensed on soot similarly promote ignition and burning by maintaining the highly dispersed soot structure prior to and after ignition.

Alternatively, Taylor and Neville(12) and later Day, et al.,(13) noted large increases in soot burning rate following deposition of soot onto surfaces previously coated with salts by evaporation. Both of these investigations concluded that the salts probably functioned by hastening the decomposition of carbon-oxygen surface complexes. With this barrier removed the carbon surface was believed to be more rapidly attacked by oxidizing gases. A brief review of the succeeding years' publications has failed to disclose any further discussion of these or other hypotheses for the action of the salts. It is of interest to note that the promotion effect is claimed either for salts vaporized onto the soot or for soot condensed (deposited) onto the previously deposited salt.

In the more recent work of Duval and coworkers(10) inorganic cations were impregnated into graphite carbon from water solution and then the rates of oxidation were noted. The results showed that the introduction of cations at 120 ppm concentration produced rates of oxidation up to 470,000 times that of the untreated graphite. In this study the effective cations were identified as representing those elements that have variable oxidation states, and can exist in defect states of oxidation. By this means they serve as oxygen carriers to the graphite interface.

The differences in relative effectiveness of the various metal salts in these two studies(9,10) seems to underline differences in mechanism of action that have occurred, either because of the difference in method of application or because of the differences in reactivity and structural stability of soot and graphite. The variable valence postulate for the catalytic action on graphite is the same as that widely used to explain the catalytic action of high-surface-area oxide catalysts in catalytic hydrocarbon oxidizers. The large increases in oxidation rate illustrated by these catalytic applications indicate that considerable catalytic assistance is available for the burning of diesel-exhaust particulate.

For the present application, the catalytic effect should start at temperatures less than that at which the unassisted thermal oxidation has been detectable and the heat release rate due to this catalytic oxidation must be sufficient to achieve the ignition temperature. In the U.S. Bureau of Mines study(9) trials of uncatalyzed ignition of furnace soot established the ignition temperature at about 615 C, and it was observed that insignificant oxidation rates were obtained below 480 C. The reduction of inlet oxygen concentration from normal air to 8 percent had little effect on the ignition temperature for untreated samples.

Both the design of the catalytic chamber and the activity of the catalyst influence the ability of any device or concept to achieve ignition. This study will attempt to define the most favorable form of catalysis and a chamber design which will maximize the repeatability of the catalytic ignition at acceptable performance levels.

Experimental Method

The reactor used in these experiments is shown in Figure 9. A sample of diesel soot, 0.15 g, is placed in a stainless steel pan that is about 10-mm wide, 47-mm long, and about 3-mm deep. One thermocouple junction, chromel-alumel 26 gauge, is buried in the sample, the other is in the gas stream just upstream of the sample. The entire quartz reactor up to the standard taper joint is placed in a tube furnace that is heated gradually from room temperature to 600 C in about 1.5 hr. During most of the heating the sample lags behind the indicated gas temperature by about 15 to 25 degrees centigrade. On ignition the sample temperature rises abruptly at a rate of 100 to 200 degrees per minute and the occurrence of ignition on some portion of the sample can be confirmed by observation of the orange-yellow glow produced as the combustion site moves through the sample. Since the gas temperature typically is rising about 5 to 10 degrees per minute, the ignition temperature can be identified with an uncertainty of only a few degrees. Typically, the indicated temperature rise, T_S-T_G, reaches a maximum of about 120 to 200 C, and this lags behind the true combustion-produced temperature rise by an amount depending on the actual location of the hot zones in the sample with respect to the thermocouple. The arrangement is sensitive to a temperature change of less than one degree so that the occurrence of ignition somewhere in the sample is detected readily. Sample traces of the temperature plots obtained during experiments are shown in Figure 10.

The air flow was held at 1 liter per minute for the first 12 runs; from Run 13 onward this flow was increased to 2 liters per minute to accommodate a few trial measurements of CO_2 production.

Catalytic salts were added to the diesel soot as methanol solutions and the solvent was removed before trial by heating the sample 16 to 24 hours at 115 to 130 C. In each case the salt solution was made up 1×10^{-5} molar so that a few milliliters of these solutions sufficed to impregnate 0.20 g of soot; after drying, 0.15 g of the sample was used for the experiment.

The soot samples used in this study were brushed from the walls of the exhaust pipe after various experiments. They were identified by the date of collection and by the engine operation data for that date.

These loose samples were extremely fluffy and it was found difficult to get good thermocouple contact with them. It was found that samples dispersed in methanol had a more suitable density after removal of that solvent at 110 to 130 C and so the uncatalyzed samples were examined in this form. Since all catalyst applications were made from methanol solution in the same way, we believe the uncatalyzed performance represents a correct blank for comparison with the catalyzed samples.

In this phase of the bench experiments the primary intent was to survey the parameters that control catalytic ignition; most of the data listed in this report were obtained using a single collection identified by the date 12/12/79. Table IV provides a comparison of that sample with a few other samples that were tried in order to compare the responses of different particulate to catalytic ignition.

Results

The activities of a few metal chlorides for promoting ignition of the diesel particulate are compared in Table V. The superiority of copper chloride is surprising in view of the relatively high oxidation activity that has been demonstrated by other investigators for catalysts based on Co, Mn, and Pt at lower temperatures than used here. In each case the question arises concerning the temperature required before a catalytic form of the metal can be obtained under the conditions used here where no preactivation treatment is employed. Persistence of some part of the water of crystallization in a few cases may be retarding the decomposition of the catalytic salt during the heating period prior to ignition.

A further investigation of the parameters controlling catalytic ignition was made by varying the anion of the salt used. Table VI shows that good performance is not limited to the chloride as indicated by the earlier U.S. Bureau of Mines study(9), presumably because in the present case volatilization of the salt is not relied upon to deposit the salt on the accumulated soot. The superiority of copper salts over the cobalt equivalents is further demonstrated in this table. Figure 11 shows that the closely competitive performance of chloride and nitrate salts of copper continues over a range of catalyst concentration.

The earlier U.S. Bureau of Mines study(9) had shown some catalytic effect for salts such as NaCl and so a series of experiments was tried with different amounts of sodium and ammonium salts added to the copper chloride solution in order to determine how such additions might affect the activity. The various trials of Table VII represent experiments in which the anion (e.g., chloride) concentration is varied over a wide range while holding the copper concentration constant, and also permits comparison of the use of Na^+ versus NH_4^+ cations. The results favor the use of Na^+ rather than NH_4^+ salts and demonstrate that substantial increase in catalytic effect results from addition of NaCl or $NaNO_3$ to the catalyst solution.

Conclusions

1. Diesel particulate is readily brought to ignition at 380 to 400 C by application of minor concentrations of metal salt solutions to the previously collected particulate. The catalytic action of the metal salt is enhanced by admixing salts such as sodium or ammonium chloride and nitrate. This represents a lowering of ignition temperature of about 150 C compared to the untreated particulate. Detectable promotion of oxidation rates is found at even lower temperatures.

2. Among the metals studied to date, copper salts work best as catalysts for particulate oxidation. The other metals, which include some known to have high catalytic activity for oxidation, exhibit low activity compared to those expected for well-activated preparations.

3. The catalytic effect of copper salts in the present application does not require the use of chlorides as noted in previous studies of furnace soot oxidation. The previous preference for chloride apparently arises because of the salt volatilization required for the furnace application.

4. The catalytic effectiveness of a metal salt in the present application may be limited by the requirements for its activation as a catalyst. Since preactivation before use is not practiced here, the facility with which the metal can achieve active form during heat-up (prior to about 350 C) is very important. The superiority of copper salts is suggested to arise for this reason.

5. The mechanism of catalytic action exhibited in this study is not known and an investigation of that mechanism is required for further clarification of the requirements for catalytic ignition of diesel particulate oxidation.

SECTION 4

FUTURE PLANS

Current and future activities on this program will include additional characterization of particulate in the exhaust system; continuation of the bench experiments on particulate oxidation characteristics and catalysis; ignition and catalytic experiments in the engine exhaust; and evaluation of devices and concepts on the engine.

For the additional particulate characterization we plan to concentrate on particulate collected by various means directly from the exhaust pipe. Mass concentration and soluble organic content will be measured under different engine operating conditions, and analytical techniques such as infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis, will be explored for their suitability to yield useful results. We also plan to conduct more surface area and carbon, hydrogen, and ash measurements.

The catalysis bench experiments will include an investigation of the mechanism of catalytic action as well as trials of a greater variety of particulate samples and simulation of exhaust conditions.

The oxidation bench experiments will be aimed at establishing a measurement methodology and using it to characterize a variety of particulate samples collected from the engine under various engine operating conditions and sampling methodologies.

In a final phase of the program, catalytic materials, techniques, and concepts studied in the bench experiments will be evaluated in the engine exhaust system. In addition, devices or concepts which emerge from the state-of-technology review will be evaluated to the extent that sufficient detailed information or actual prototype devices can be obtained. The objective of these on-engine evaluations will be to establish potential feasibility of concepts not to develop prototype systems.

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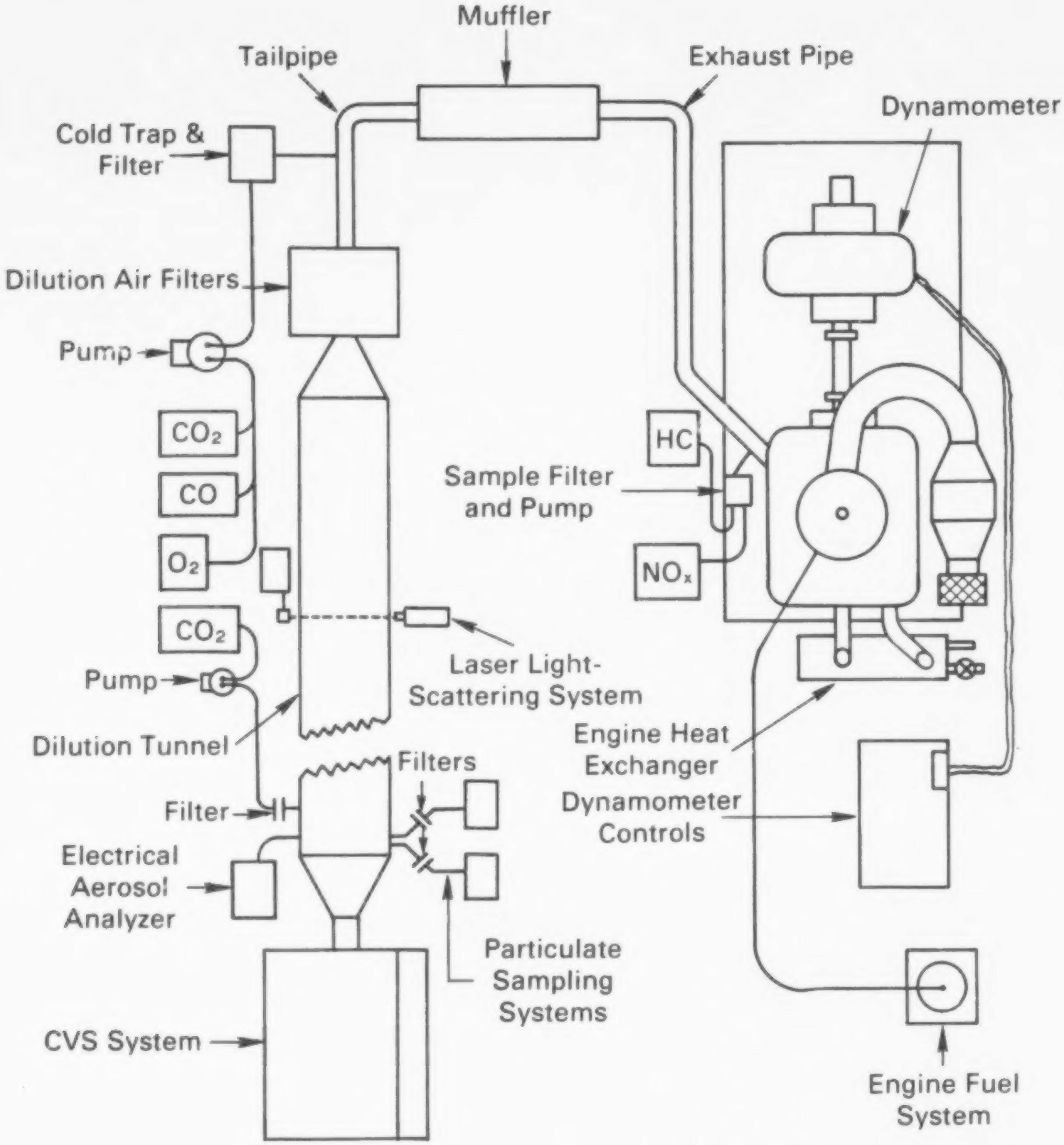

Muffler
Tailpipe
Exhaust Pipe
Dynamometer
Cold Trap & Filter
Dilution Air Filters
Pump
CO₂
CO
O₂
CO₂
Pump
HC
Sample Filter and Pump
NOₓ
Laser Light-Scattering System
Dilution Tunnel
Engine Heat Exchanger
Filters
Filter
Dynamometer Controls
Electrical Aerosol Analyzer
Particulate Sampling Systems
CVS System
Engine Fuel System

FIGURE 1. ENGINE EXPERIMENTAL FACILITY

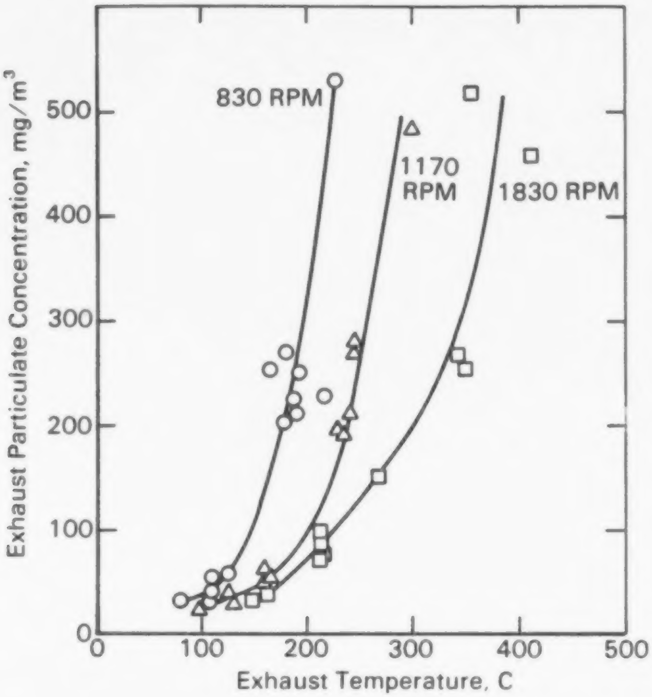


FIGURE 2. INFLUENCE OF EXHAUST TEMPERATURE AND ENGINE SPEED ON PARTICULATE EMISSIONS CONCENTRATION

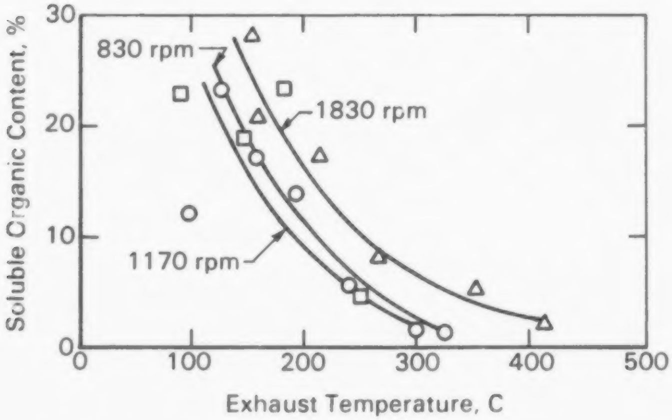


FIGURE 3. INFLUENCE OF EXHAUST TEMPERATURE AND ENGINE SPEED ON SOLUBLE ORGANIC CONTENT

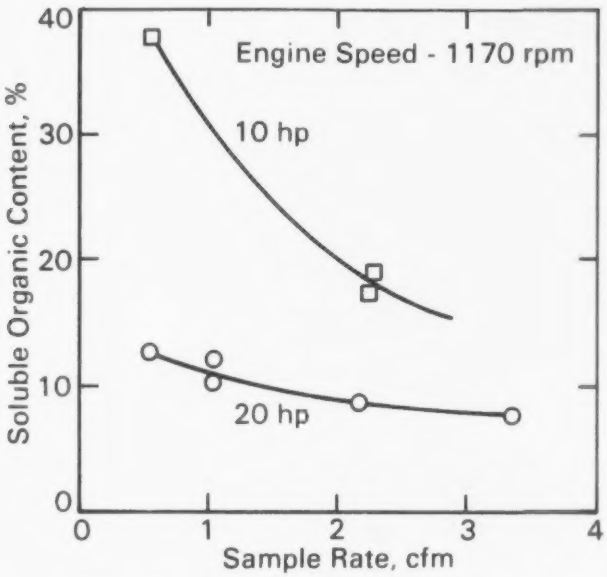


FIGURE 4. EFFECT OF SAMPLING RATE ON SOLUBLE ORGANIC CONTENT MEASUREMENT

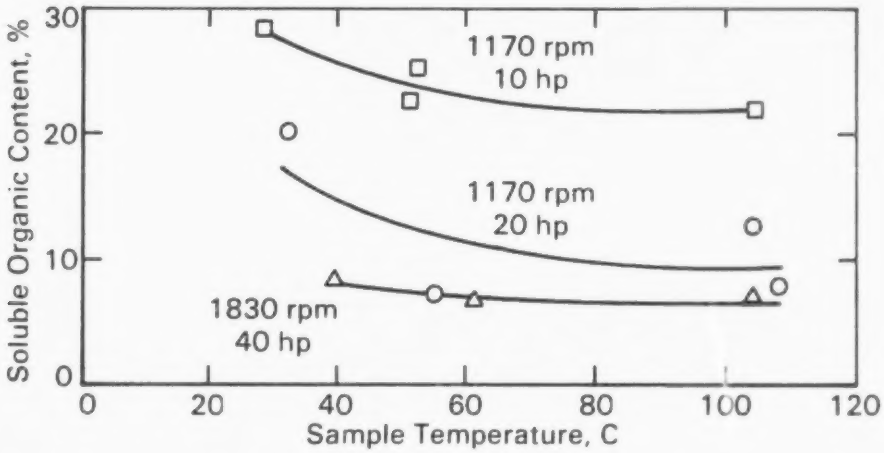


FIGURE 5. EFFECT OF SAMPLE TEMPERATURE ON SOLUBLE ORGANIC CONTENT MEASUREMENT

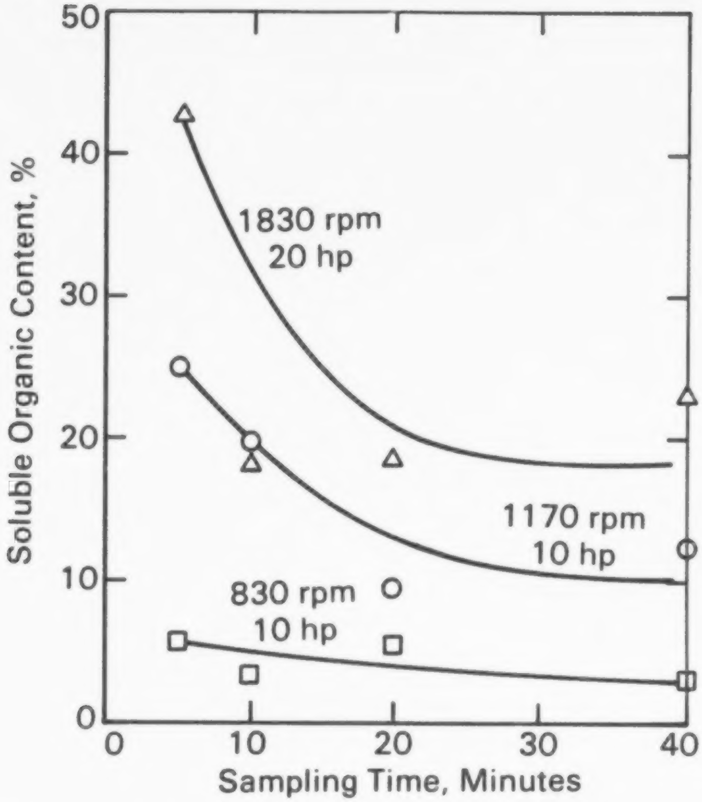


FIGURE 6. EFFECT OF SAMPLING TIME ON SOLUBLE ORGANIC CONTENT MEASUREMENT

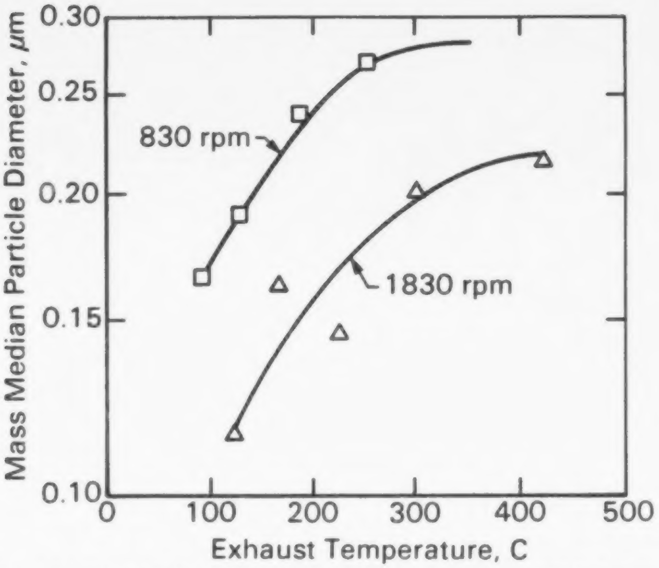


FIGURE 7. INFLUENCE OF EXHAUST TEMPERATURE AND ENGINE SPEED ON PARTICULATE MASS MEDIAN DIAMETER

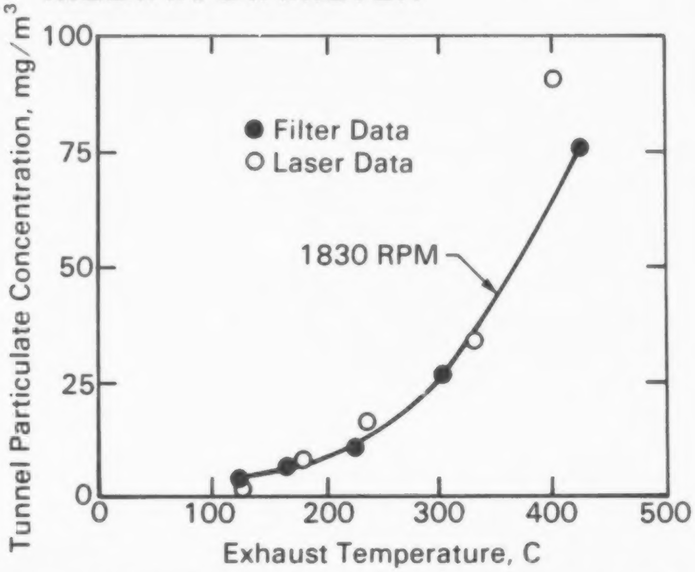
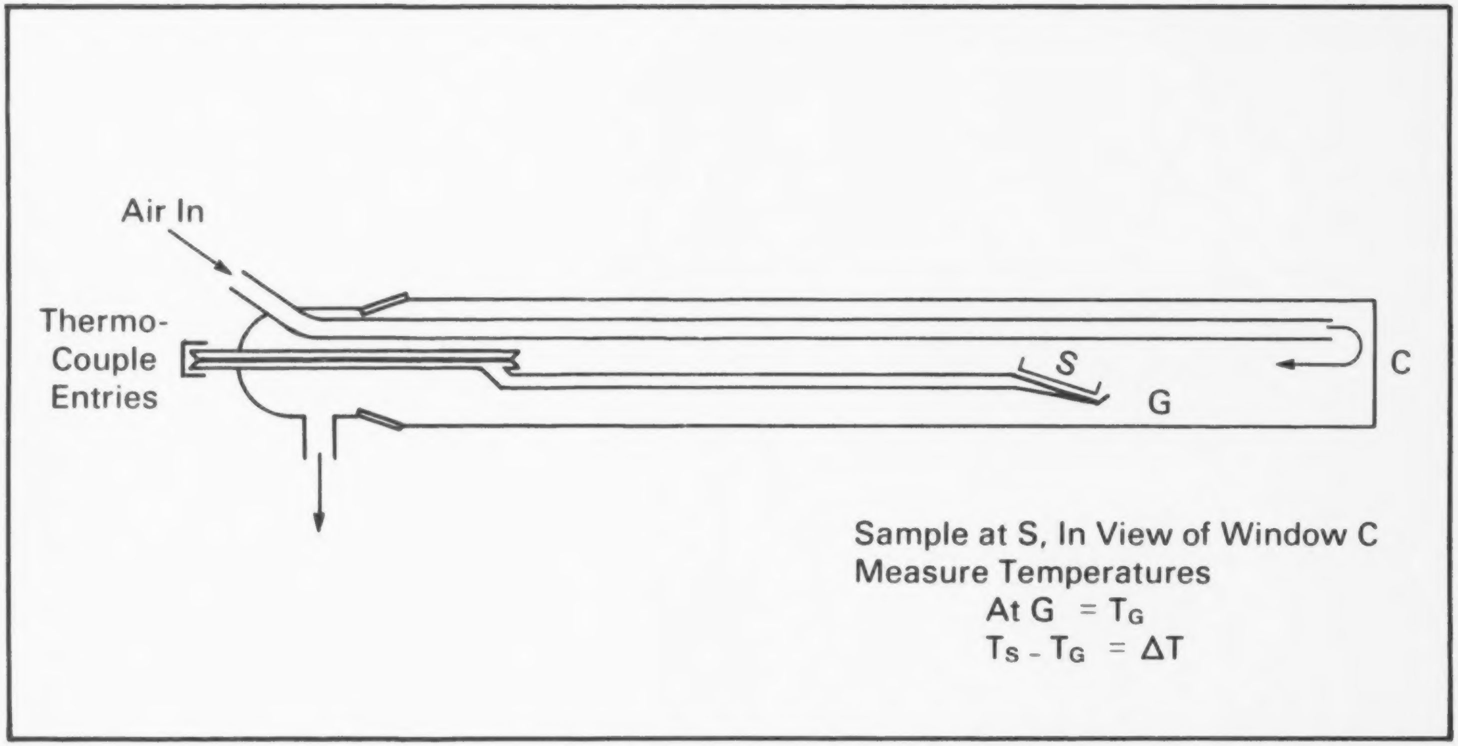
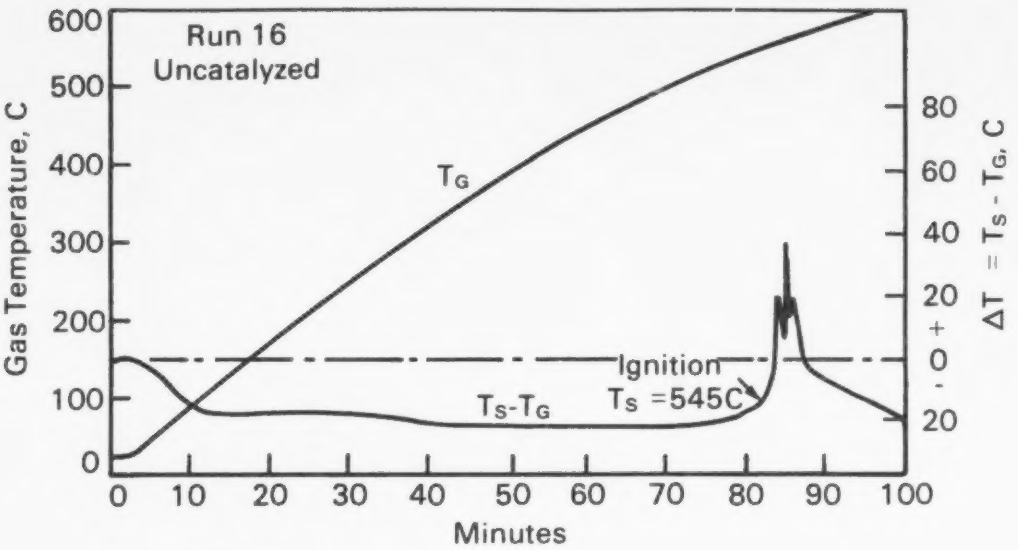


FIGURE 8. COMPARISON OF FILTER AND LASER PARTICULATE MASS CONCENTRATION DATA


Air In
Thermo-Couple Entries
S
G
C

Sample at S, In View of Window C
Measure Temperatures
At G $= T_G$
$T_S - T_G = \Delta T$

FIGURE 9. ARRANGEMENT OF QUARTZ REACTOR FOR MEASUREMENT OF IGNITION TEMPERATURES



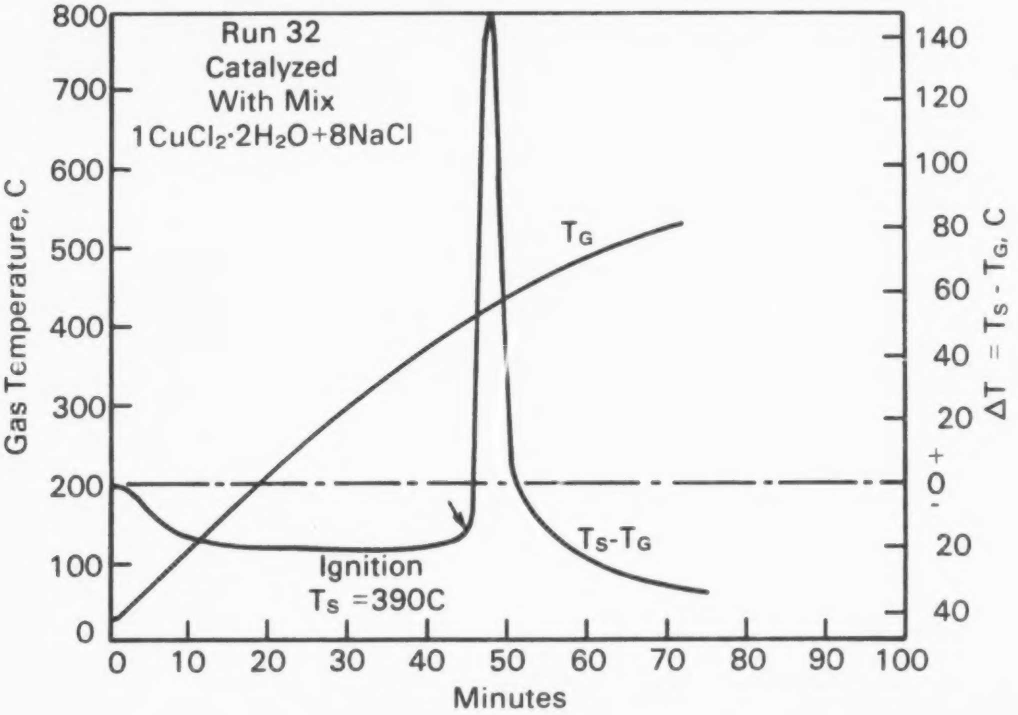


FIGURE 10. SAMPLE TEMPERATURE TRACES DURING IGNITION TRIALS

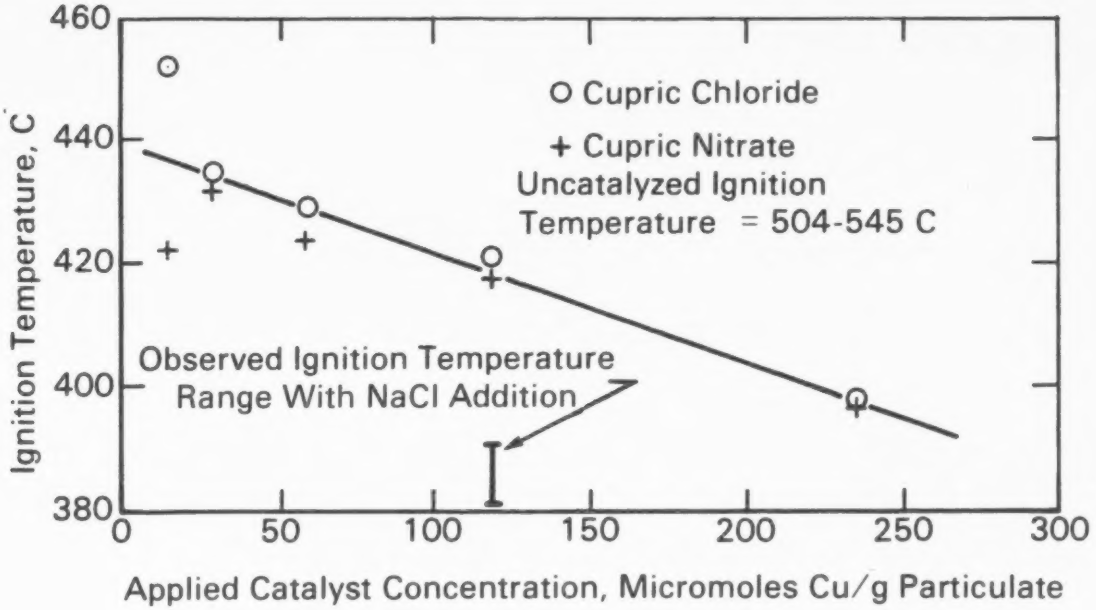


FIGURE 11. EFFECT OF SALT CONCENTRATION ON IGNITION TEMPERATURES

TABLE I. ROAD LOAD ENGINE OPERATION

	Test Number								
	1	2	3	4	5	6	7	8	9
Road Speed, mph	25	25	25	35	35	35	55	55	55
Engine Speed, rpm	830	830	830	1170	1170	1170	1830	1830	1830
Engine Bhp	2.08	4.15	10.4	4.97	9.94	19.9	10.1	20.1	40.3
Bsfc, lb/bhp-hr	1.44	0.89	0.56	0.88	0.58	0.47	0.63	0.55	0.43
Exh Man Temp, C	112	129	179	108	164	249	164	218	345
Tailpipe Temp, C	86	95	127	104	126	183	136	174	267
HC, ppm C	198	155	95	75	97	85	73	75	63
NO_x, ppm	117	138	185	189	238	152	210	255	335
CO, ppm	267	298	315	305	237	406	154	155	365

TABLE II. CHARACTERISTICS OF LOOSE PARTICULATE SAMPLES

Sample Date	Speed/Load Condition, rpm/hp	Soluble Organic Content, wt %	H wt %	C wt %	Ash wt %	Exh(a) Temp, C	Filter(a) Soluble Organic Content, wt %
10/25/79	1170/10	--	--	--	--	(162)	
11/15/79	1170/5, 10, 20	6.7	--	--	--	213	15
11/16/79	830, 1170, 1830/10	9.0	--	--	--	170	18
12/12/79	1170/20	10.5	--	--	--	240	16
12/19/79	1170/10	7.7	--	--	--	162	16
1/23/80	1170/5	7.2	2.0	77.1	2.0	120	20
1/24/80	1830/40	6.5	0.4	77.8	1.0	350	3
2/6/80	830/variable	2.7	0.4	70.0	0.8	182	12
2/7/80	1830/variable	5.1	1.0	89.6	2.0	240	14
2/8/80	1170, 1830/variable	1.9	0.5	82.0	0.9	220	12
2/14/80	1170/10, 20	1.8	0.5	71.0	0.6	200	12
2/15/80	1170, 1830/20	4.8	0.7	71.9	1.5	225	7
4/24/80	830/variable	--	--	--	--	(180)	
4/25/80	1830/variable	--	--	--	--	(240)	

(a) At same or similar conditions.

TABLE III. MASS SPECTROGRAPHIC ANALYSIS OF PARTICULATE SAMPLES

	Sample Designation(a)			Sample Designation(a)	
Element	11/8/79(b)	11/9/79B(c)	Element	11/8/79(b)	11/9/79B(c)
Li	10	10	Ag	<2	<2
Be	<0.05	<0.05	Cd	<3	<3
B	10	3	In	<1	<1
C	Major	Major	Sn	<3	<3
F	3	<3	Sb	<2	<2
Na	500	500	Te	<2	<2
Mg	150	150	I	0.5	<0.5
Al	1500	1500	Cs	<1	<1
Si	3000	1500	Ba	30	30
P	~1%	~2%	La	<1	<1
S	~4%	~1%	Ce	<0.5	<0.5
Cl	50	50	Pr	<1	<1
K	100	50	Nd	<3	<3
Ca	3000	3000	Sm	<3	<3
Sc	<3	<3	Eu	<2	<2
Ti	300	3	Gd	<3	<3
V	0.3	0.3	Tb	<1	<1
Cr	500	300	Dy	<3	<3
Mn	500	300	Ho	<2	<2
Fe	~30%	~10%	Er	<3	<3
Co	5	3	Tm	<3	<3
Ni	150	150	Yb	<3	<3
Cu	1500	1000	Lu	<1	<1
Zn	2000	1500	Hf	<3	<3
Ga	<1	<1	Ta	<3	<3
Ge	<2	<2	W	3	<3
As	<0.5	<0.5	Re	<2	<2
Se	<2	<2	Os	<3	<3
Br	<1	<1	Ir	<3	<3
Rb	<5	<5	Pt	<3	<3
Sr	3	0.5	Au	<1	<1
Y	<0.5	<0.5	Hg	<5	<5
Zr	<2	<2	Tl	<2	<2
Nb	<0.5	<0.5	Pb	30	30
Mo	<3	<3	Bi	<1	<1
Ru	<2	<2	Th	<1	<1
Rh	<0.5	<0.5	U	<1	<1
Pd	<3	<3			

(a) Values given in ppm unless otherwise noted.

(b) 830 rpm/2 hp.

(c) 1830 rpm/40 hp.

TABLE IV. COMPARISON OF PROPERTIES OF DIESEL PARTICULATES AND OTHER CARBONS

Sample Identification	Surface Area, m^2/g	Soluble Organic Content, wt % as rec'd	Hydrogen, wt % as rec'd	Ignition Temperature, C(a)	
				As Rec'd	Catalyzed
Diesel particulate 10/25/79	100	--	--	468	370
Diesel particulate 21/12/79	--	10.2	--	504-545	413-421
Diesel particulate 1/23/80	--	7.2	2.0	485	400-423
Diesel particulate 1/24/80	--	6.5	0.4	466	395
Ultra-F, high purity graphite	10	Nil	Nil	660	635
Cabot CSX-150	~1100	--	--	495	428

(a) In each case the sample has been slurried in methanol, then dried. For the catalyzed trials, cupric chloride was dissolved in the methanol and added to the extent of 1.18×10^{-4} mole/g soot.

-- Not measured.

TABLE V. COMPARISON OF IGNITION TEMPERATURES FOR VARIOUS METAL CHLORIDES

Run	Catalytic Salt Used(a)	Ignition Temperature, C	Maximum Temperature Rise,(d) ΔT C
16 and 38	None(b)	504-545	50-121
44	$MnCl_2 \cdot 4H_2O$	456	125
45	$CoCl_2 \cdot 6H_2O$	461	122
36	H_2PtCl_6(c)	455	237
13	$CuCl_2 \cdot 2H_2O$	421	139

(a) The salt used in each case was equivalent to 1.18 x 10^{-4} moles of the metal per gram of particulate. Since each was added in methanol and then dried at 110 to 130 C, the water of crystallization probably was lost on drying.

(b) Diesel particulate collected 12/12/79, slurried in methanol, and dried 110 to 130 C.

(c) In methanol-ethanol, not previously activated to decompose the salt other than the 110 to 130 C drying conditions.

(d) This is not the combustion temperature, but the overall maximum rise sensed by thermocouple reflecting the relative rate and completeness of oxidation.

TABLE VI. COMPARISON OF THE EFFECT OF THE ANION ON THE ACTIVITY OF THE CATALYST

Run	Catalytic Salt Used[a]	Ignition Temperature, C	Maximum Temperature Rise,[b] ΔT C
13	$CuCl_2 \cdot 2H_2O$	421	140
14	$Cu(NO_3)_2 \cdot 3H_2O$	418	165
15	$CuSO_4 \cdot 5H_2O$	432	135
45	$CoCl_2 \cdot 6H_2O$	461	122
33	$Co(NO_3)_2 \cdot 6H_2O$	469	121

(a) In each case the salt used was equivalent to 1.18×10^{-4} mole metal/g soot.

(b) This is not the combustion temperature, but the overall maximum rise sensed by thermocouple reflecting the relative rate and completeness of oxidation.

TABLE VII. EFFECT OF THE ADDITION OF SODIUM AND AMMONIUM SALTS TO THE COPPER CHLORIDE CATALYST SOLUTION

Run	Catalytic Salt Used(a)	Ignition Temperature, C	Maximum Temperature Rise,(c) ΔT C
16 and 38	None(b)	504-545	50-121
13	$CuCl_2 \cdot 2H_2O$	421	140
25	$2NH_4Cl \cdot CuCl_2 \cdot 2H_2O$	428	165
26	$2NH_4NO_3 \cdot CuCl_2 \cdot 2H_2O$	435	178
28	$2NaNO_3 \cdot CuCl_2 \cdot 2H_2O$	397	175
27	$2NaCl \cdot CuCl_2 \cdot 2H_2O$	381	184
29	$1NaCl \cdot CuCl_2 \cdot 2H_2O$	407	169
31	$4NaCl \cdot CuCl_2 \cdot 2H_2O$	391	143
32	$8NaCl_2CuCl_2 \cdot 2H_2O$	390	162

(a) The formula represents the nominal molar ratios of ingredients dissolved in the methanol solvent before addition to the diesel particulate. In each case, the copper concentration was 1.18×10^{-4} mole/g particulate.

(b) Slurried with methanol, then dried.

(c) This is not the combustion temperature, but the overall maximum rise sensed by thermocouple reflecting the relative rates and completeness of oxidation.

SINGLE-CYLINDER TESTS OF EMISSION CONTROL METHODS FOR LARGE-BORE STATIONARY ENGINES

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ABSTRACT

The research work presented herein was undertaken in order to develop combustion modifications which substantially reduce NO_x emissions of large-bore engines, without significantly increasing fuel consumption of carbonaceous emissions. The scope of the project covers NO_x control technology for diesel and spark ignition engines, bore sizes ranging from 8 to 20", and both 2 and 4 cycle charging methods. The current status of the project permits us to report the results of 40% of the Phase III experimental tests. In Phases I and II, a compendium of 30 emission control methods was prepared, and an evaluation procedure was used to screen down the list to the 12 methods which are now being tested in Phase III.

Cooper Energy Services utilized a 20" bore, 330 rpm single cylinder engine to test the effect of unmixedness (modified fuel gas injection) and conventional "tuning" methods (timing, equivalence ratio, spark location, gas valve location, and piston shape). The principal finding was that NO_x emissions are more sensitive to air-fuel ratio than any other variable, giving a factor of five reduction as the equivalence ratio was leaned out from $\phi \simeq .76$ to $\phi \simeq .62$. The practical implication is that spark gas engine emissions are limited primarily by turbocharger efficiency and the combustion lean limit. Rate of heat release analysis confirmed that a reduction in fuel-air ratio produces longer ignition delay and lower flame speed. Gas valve modifications degraded NO_x; piston shape had more effect on NO_x than either gas valve or spark plug location.

Fairbanks Morse conducted tests of pilot injection and increased rate of injection on an 11" bore model PA-6 engine at 1,000 rpm. At 9 g/bhp-hr the baseline NO_x is characteristic of this class of engines. Retarded timing increases BSFC 1.1% and decreases NO_x 4% per degree crank angle. Exhaust temperature was found to limit the NO_x reduction achievable with either pilot injection or injection rate at full load; however, at part load NO_x reductions of 20% were found for both methods with some BSFC improvement. Analysis of derived heat release profiles show that the "spike" observed for high speed diesels does not appear for the PA-6 engine.

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ACKNOWLEDGEMENTS

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SECTION 1

INTRODUCTION

Large-bore stationary engines are a significant source of NO_x emissions in the United States. Primarily used in pipeline transmission and compression of natural gas, oil drilling, and electric power generation, this class of engines accounts for 1.5% of U. S. fuel usage, as shown in Table I. Covering a power range from 100 to 750 hp per cylinder, and a speed range from 300 to 1200 rpm, this engine class includes both diesel and spark ignition types. Most large-bore engines are turbocharged in order to reduce fuel consumption.

Emissions control efforts for large-bore engines are limited to NO_x, since the emissions of carbon-containing species (CO, HC, soot) are relatively low and the conventional engine fuels nearly sulfur-free. As shown in Table II, the NO_x emission rate of these engines is significantly higher than any other major combustion device for a given amount of fuel, and is almost a factor of six greater than the coal-fired utility boiler (which is the stationary source of greatest concern). This remarkably high NO_x emission rate is caused by four factors:

- Compression preheating to 800°K increases flame temperature;
- Low heat loss during combustion maintains high flame temperature;
- Air-fuel ratio in the 18-20 range which maximizes NO_x; and
- Low rpm results in 10-20 msec at peak temperature.

In certain portions of the combustion chamber, the flame temperature is so high that the NO_x level reaches equilibrium (8,000-12,000 ppm) and then begins to decrease by the reverse of the Zeldovich mechanism as the gas cools by expansion.

The outlook for emission standards for large-bore engines is uncertain at this writing because of fast-changing control technology. In July 1979, the EPA proposed NO_x emission ceilings corresponding to 40% reduction from the typical level, as shown by Figure 1. These standards as proposed would come into effect in 1982. However, while these standards were being formulated and reviewed, examples of new control technology (e.g., torch-ignition for spark gas engines and catalyzed reduction of NO_x by ammonia) began to be investigated by several engine manufacturers. Recently, the California Air Resources Board issued a model rule based on catalyst technology which calls for a 90% NO_x reduction by as early as 1983, contingent on the successful demonstration of control technology. Apart from the question of emission standards, engine manufacturers are experiencing incentives for low NO_x emissions due to PSD requirements. As shown in Figure 2, the installation of a 5,000-hp engine station will require an NO_x emission rate of 5 g/hp-hr (which is equivalent to about a 60% reduction from uncontrolled levels) in order to avoid a lengthy PSD review process.

The promise of recent developments reflects two basic premises concerning the NO_x level of large-bore engines:

(1) There is substantial potential for NO_x reduction.

(2) The actual levels of NO_x which are feasible can only emerge after extensive experimental and field test work.

The EPA program described below is aimed at this experimental test work.

SECTION 2

PROGRAM DESCRIPTION

The objective of the present program is to develop a technical foundation for substantial reduction of NO_x emissions of representative large bore engines, without degradation of fuel economy. As the program has evolved, it now appears reasonable to target for 50-60% NO_x reduction with less than 3% penalty in fuel consumption. Table III shows the four major phases of work, starting with the identification of various emission-control methods and ending with field tests on full scale engines. Currently, Phase III is about 40% complete, and the results of the first four methods of NO_x control are reported herein:

Spark	Diesel
• Piston shape, gas valve, and spark location	• Pilot injection
• Altered gas valve	• High injection

The NO_x control methods which are being tested for spark-ignition engines fall into four categories, as follows:

(1) Reduced temperature
(2) Leaner combustion
(3) Stratified combustion
(4) Exhaust gas treatment

Figure 3 illustrates the mechanisms by which NO_x production is altered in Categories (1)-(3) above. The contours labelled 1, 10, 100, and 1000 ppm/msec define a steep surface of increasing NO_x production rate. Normally, a hot gas element follows the path labelled "conventional," starting at about 2400°K flame temperature and increasing to 2600°K or more due to compression. This produces NO_x at a rate well above

1000 ppm per millisecond as illustrated by the contours on Figure 3. The "reduced temperature" methods simply shift this path to the left (about 100°K lower) where the NO_x production rate is much lower. The "lean combustion" methods force the combustion to begin and proceed at lower fuel-air ratio ($\phi \simeq 0.7$) where the NO_x production rate is reduced. The "stratified combustion" method creates a lean and rich zone, thereby avoiding the $\phi = 0.8$-0.9 regime (where NO_x production is at a maximum). This brief discussion provides some background on the methods which are being tested in Phase III for spark gas engines.

For diesel-engine NO_x control, the approach which has guided our Phase III plans is to retard the fuel injection process and compensate for the delayed burning by:

- Reduced ignition delay, and/or
- Increased mixing rate.

Normally, retarded timing causes unacceptable penalties in fuel consumption, and often results in excessive exhaust temperature and soot levels. Therefore, it is essential for NO_x control to make the latter stages of the combustion process more vigorous in order to allow the early stages to be retarded and less intense.

Table IV presents the 12 NO_x-control methods which were selected for testing in Phase III. The process of selection was based on the projected NO_x reduction, the projected cost of control (per horsepower), and the feasibility. The relative ranking of the concepts by two of these criteria is illustrated in Figure 4, in which the threshold for Phase III selection is shown as a dashed line starting at 20% NO_x reduction, and requiring greater NO_x reductions above $30/hp ten-year cost impact.

SECTION 3

SPARK IGNITION ENGINE TESTS

A. EXPERIMENTAL ARRANGEMENTS

The tests were conducted using a Cooper Model Z330 single-cylinder, two-stroke engine of 20" bore and 20" stroke dimensions, 681-hp rated power at 130 bmep and 330 rpm. Gas fuel is injected directly into the cylinder during the compression stroke, and the resulting mixture is ignited by two spark plugs nominally firing at 7° before top center. Figure 5 shows the air and fuel supply piping and controls in schematic; the air manifold pressure and temperature could be controlled independently. Figure 6 is a photograph illustrating the general layout of the experimental facility. The large cylinder is the plenum in the air supply used to dampen air pressure fluctuations.

Emissions samples were taken from the following three points, as shown in Figure 7:

(1) Exhaust stack (diluted with scavenging air);

(2) Exhaust port (undiluted--see Figure 8); and

(3) Cylinder contents during combustion ("Cox valve").

Samples were analyzed for NO/NO_x, THC, CO, CO_2, and O_2 by conventional methods (chemiluminescent, FID, NDIR, and paramagnetic analyzers, respectively). The fuel-air ratio of the trapped gas is essentially unknown for a scavenged 2-stroke engine. This problem was solved by mounting a poppet valve at the exhaust port as shown in Figure 8. The valve was actuated by the flow of high pressure exhaust gas (undiluted by scavenging air).

Natural gas was used throughout the experiments; the composition varied slightly as shown in Table V.

In order to provide additional diagnostic information about the combustion process, the cylinder pressure traces were averaged for several hundred consecutive cycles. The time-resolved rate of heat release in the cylinder was calculated from each averaged pressure trace by a thermodynamic computer program.

B. BASELINE DATA AND THE EFFECT OF FUEL-AIR RATIO

The NO_x emissions of the engine in its normal configuration were obtained for several spark timings and air-fuel ratios in order to establish a baseline or reference for further tests. All runs were made at rated power and speed (130 bmep and 330 rpm). The results, presented in Figure 3, show that the air-fuel ratio affects NO_x markedly, reducing NO_x a factor of five (from 25 to 5 g/bhp-hr) as the mixture is leaned out from a fuel-air equivalence ratio of 0.76 to 0.62. Retarded spark timing also reduces NO_x, giving about a 25% NO_x change for a timing shift of 4° crank angle (6% per degree).

The steepness of the NO_x vs ϕ graph, which is characteristic of all premixed combustion systems, suggests that the most fruitful approach for low NO_x is to lean out the mixture. Several limits are encountered, however, as the mixture is shifted to lower fuel/air ratio:

- Misfire Limit: Positive, reproducible ignition becomes more difficult to achieve very lean mixtures. The flame may begin to propagate away from the spark plug, but falter or travel at low flame speed. The first sign of misfire is increased variation in peak cylinder pressure. Instrumentation on the Z330 single-cylinder engine automatically calculates the standard deviation in peak pressure (σ), which is normally in the 60-90 psi range for satisfactory ignition. In the 90-120 psi range, some misfire is first noticed but engine operation may be marginally feasible. Above about 120-130 psi, misfire is definitely unacceptable. For the baseline engine, Figure 9 shows $\sigma = 90$ psi reached at about $\phi = 0.62$ to 0.66.

- Late or Incomplete Combustion: Flame propagation is slower for very lean mixtures. This leads to penalties in fuel consumption and CO/HC emissions due to pockets of mixture which are partially unburned. Notice in Figure 9 that the bsfc increases as the fuel-air equivalence ratio is extended below about $\phi = 0.65$.
- Turbocharger Capacity Limit: In any shift to higher air-fuel ratio, in order to maintain power, the fuel flow cannot be reduced. Instead, the air pressure must be increased; but the ability of the engine to supply itself with high pressure air is limited. For a typical spark gas engine, turbocharger efficiency is limited to about 64%, which ultimately limits the fuel-air ratio.

The emphasis of the EPA experimental program is on finding means to overcome the misfire limit.

C. EFFECT OF PISTON SHAPE, GAS VALVE LOCATION, AND SPARK PLUG LOCATION

Prior to the tests of specific NO_x control methods, an attempt was made to find out if the baseline engine configuration was optimum with respect to the choice of piston and the location of gas valve and spark plugs. Manufacturers often vary these components in order to "tune" an engine for best fuel consumption and emissions. The matrix for these "conventional" techniques is given in Table VI, which shows systematic timing variations for each combination tested.

Three piston shapes (shown in Figure 10) were tested, and the results are given in Figure 11. Apparently, substitution of the "tee-pee" piston increased fuel consumption from 6,750 to 6,950 Btu/bhp-hr (a 3% penalty). The "Mexican Hat" piston and the flat top (baseline) piston give almost identical performance, except that the Mexican Hat piston may allow slightly leaner operation without misfire (see Figure 11, top set of curves). If 110-psi pressure variation were to be taken as the misfire limit, the baseline piston would be limited to about 8 g/bhp-hr NO_x at $\phi = 0.66$ compared to the Mexican Hat at 6 g/bhp-hr NO_x at $\phi = 0.63$.

The locations of the spark plug pairs and the gas valve are shown in Figure 12. Variations in the location of these components made very little difference in NO_x or bsfc with proper timing adjustments, as shown in Figure 13. The center spark (open symbols in Figure 13) allowed leaner operation without misfire (σ below 120 psi).

In summary, the baseline engine configuration with flat top piston, center spark plugs, and center gas valve appears to be relatively well "tuned" with respect to NO_x and bsfc. This configuration was used as the baseline standard for the remainder of the tests.

D. EFFECT OF GAS VALVE DESIGN

In a gas-injected engine, the mixture at the time of ignition may contain incompletely mixed pockets. The number, size, and composition of these pockets depends in part on the initial fuel gas dispersion achieved by the gas valve. The standard gas injector is an outward opening pintle valve of 1-1/8 in throat diameter (.405 sq-in annular throat area). This design was altered, as shown in Figure 14, in order to explore the effect of fuel gas dispersion (local stratification) on NO_x emissions and fuel consumption.

The results are shown in Figure 15. It is interesting to note the change in slope of the NO_x vs ϕ curves as the gas valve throat diameter increases from 1.13" (○, ●, ▲) to 1.31" (⊙) and then to 2.13" (□). The flatter curves for a larger gas valve can be explained in terms of differences in the extent of mixing at the time of combustion: It is known that poorly-mixed fuel-air mixtures produce a constant amount of NO_x per unit fuel, no matter how much extra air is present. This is because the extra air does not mix with isolated fuel pockets and therefore does not affect the flame temperature. In Figure 15 the very large gas valve presumably resulted in this type of fuel-pocket combustion and a flat NO_x vs ϕ curve. By contrast, the well-mixed combustion produced by a small gas valve is very responsive to any additional air (lower ϕ) because the additional air lowers the flame temperature.

As a result, the NO_x level can be increased but not decreased by changing the gas valve design on the Z330 engine. The existing gas valve appears to be nearly optimized in that it produces a very homogeneous mixture. Reducing the gas valve area from the baseline (.405 sq. in) may slightly reduce misfire (see the top set of curves in Figure 15) and thereby extend the lean limit of operation.

E. ANALYSIS OF THE RATE OF HEAT RELEASE

For each run, the rate of heat release in the cylinder was calculated from a smoothed pressure trace. The rate of heat release is determined by and therefore gives information about the ignition delay, the rate of flame area growth in the early stages of combustion, and the rate of burning in the critical late stage of combustion as residual pockets of flammable mixture are reached by the flame and consumed. Figure 16 illustrates typical rate-of-heat-release curves for two runs made at 5° and 9° spark timing. Note that the two curves have essentially the same triangular shape, but are shifted by about 4° (as expected). The combustion duration is just under 40° crank angle. The rate of heat release is sharply peaked, with the maximum heat release occurring at the point of greatest flame area and rate of flame travel. This probably occurs just as the flame (visualized as an irregular hemisphere propagating toward the piston) first reaches the wall. The front of the triangle is steep, the slope proportional to the average flame speed. The back of the triangle is dependent on the chamber geometry, which affects the flame area reduction. The "tail" represents the consumption of residual unburned gas and is critical to the fuel consumption performance.

Recall that the fuel-air ratio, ϕ, has a marked effect on the NO_x emission. The rate of heat release analysis provides insight on how the combustion process is affected by changes in ϕ. As seen in Figure 17, successive reductions in ϕ cause four changes:

- Triangle starts later (longer ignition delay);
- More gradual front side of the triangle and peak reached later (slower flame speed);
- Lower peak (lower maximum burning rate); and
- Longer "tail" (longer combustion duration)

Further analysis of the shape of the rate of heat release is being conducted. Apparently the NO_x level can be correlated with the slope of the front side of the triangle (flame speed). As further data becomes available, we will attempt to construct a function $f(\alpha,\beta)$ of the same form as the rate of heat release and correlate the parameters α, β with operating conditions of the engine.

F. FORTHCOMING SPARK IGNITION TESTS

In the forthcoming tests, lean-burn methods such as torch-ignition and multiple spark will be tested. These methods show promise of up to 70% NO_x reduction, not only based on the baseline data on the Z330 single-cylinder engine, but also based on data presented by Helmich (1979) and Chrisman (1980), as shown in Table VII. The research needs for torch ignition which will be addressed by the EPA project include the following:

- Methods of metering the amount of fuel in the torch chamber in order to optimize torch fuel-air ratio.
- Systematic study of the effects of torch shape and direction, by changing nozzle diameter, nozzle shape, nozzle length, and orientation of the axis.

In addition ammonia/catalyst systems for exhaust gas treatment will be tested. The research needs for these systems include the following items:

- Control systems for catalyst temperature
- NH_3 carryover detection
- Platinum vs base metal
- Catalyst life (extended tests)
- Optimum space velocity
- Corrosion from sulfates (which form from the reaction of SO_3 traces with NH_3

SECTION 4

DIESEL ENGINE TESTS

A. EXPERIMENTAL ARRANGEMENTS

The tests of diesel engine methods were carried out on an 11" bore four-stroke turbocharged single-cylinder engine, the Model PA-6 of S.E.M.T. design. The characteristics of this engine are as follows:

- Displacement, 1090 in^3
- Compression ratio, 11.8/1
- Rated power, 350 hp* at 1000 RPM
- Brake mean effective pressure, 270 psi
- Injection: 20-mm plunger, 8 x .50 mm holes
- Piston shape: Mexican hat
- Standard timing: 23.5 btdc

Figure 18 gives a cutaway view of the entine. Manifold air temperature and pressure can be controlled independently as in the Cooper facility described above. The emissions and cylinder pressure instrumentation is also comparable, with the exception that only exhaust sampling is done for the diesel tests.

B. BASELINE CHARACTERISTICS AND THE EFFECT OF TIMING

The NO_x emissions and fuel consumption of the PA-6 are strongly influenced by the timing of the start of fuel injection, as shown in Figure 19. The NO_x can be reduced from 9 to about 6 g/bhp-hr by retarding injection from 18 to 11° btdc (4.5% per degree). However, exhaust temperature is excessive and there is a substantial fuel penalty. Attendant to the NO_x reduction is a fuel penalty of about 1.1% per degree of retardation on the average.

---

*Equivalent to 400 hp on multicylinder engine.

These characteristics are representative of large-bore diesel engines and the engine seems to be appropriate as a test facility. The scatter in NO_x data for replicate runs is ±0.5 g/bhp-hr or about ±5%.

C. PILOT INJECTION

Pilot injection was tested in an attempt to compensate for the undesirable side effects of retarded timing. The pilot quantity was varied from 4 to 12% of the total fuel per cycle, and four pilot advances were tested (40, 60, 80, and 120° btdc). Figures 20 and 21 show the results for full load and part load, respectively. The solid line represents the baseline (no pilot) case. At full load, pilot injection did not improve the BSFC-NO_x characteristics. Retarded timing beyond 19.5° btdc was not possible because of exhaust temperature limitations.

However, at part load, certain configurations of pilot injection improved BSFC by up to 6% at fixed timing. Apparently pilot quantity should be minimized unless timing is retarded. With retarded timing at part load (Figure 21), NO_x may be reduced by about 20%. Results were inconsistent, however.

In summary, pilot injection did not give significant NO_x reductions except in special cases. The pilot system was not matched to the injector and this may have limited its potential NO_x effect.

D. INCREASED INJECTION RATE

The intent of increased injection rate, like pilot injection, is to allow retarded timing without undesirable side effects such as smoke excessive fuel consumption, or high exhaust temperature. Figure 22 illustrates the difference in fuel injection schedule between the standard injector (20 mm plunger, 8 x .50 mm nozzle) and a high-rate injector (24 mm plunger, 9 x .55 nozzle). The larger injector has a higher average fuel pressure and a shorter injection duration. Eight combinations of plunger and nozzle were tested, as shown in Table VIII.

The results for full load (350 hp) and part load (234 hp) are presented in Figures 23 and 24, respectively. It is clear that unless timing is retarded, the increased injection rate acts to increase NO_x instead of reducing it. With retarded timing, increased injection rate is beneficial but the NO_x response is mixed:

(a) Full load - no improvement in NO_x-bsfc.

(b) Part load - up to 20% NO_x reduction at fixed bsfc; and 30% NO_x reduction if a bsfc penalty of 3% is permissible.

The best injection system appeared to be the combination of the 24 mm plunger and 8 x 0.6 mm nozzle.

REFERENCES

1. Helmich, M. J., "Clean Burn Engine," paper presented at the AGA Transmission Conference, New Orleans, Louisiana, May 1979.
2. Chrisman, B., "Exhaust Emissions Regulations and Control Technology," paper presented at the 27th Annual Meeting of the Gas Compressor Institute, Liberal, Kansas, April 1980.

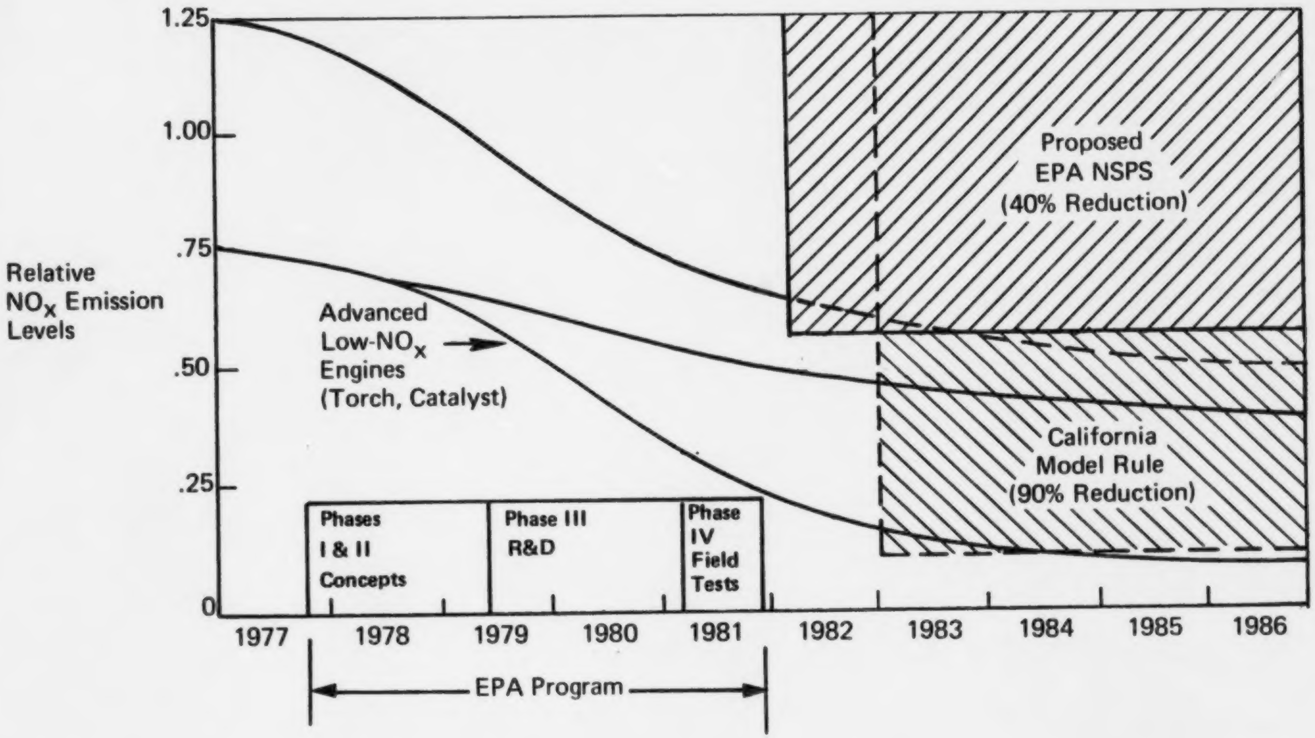

Figure 1. Scenario of the development of large-bore engine emissions.

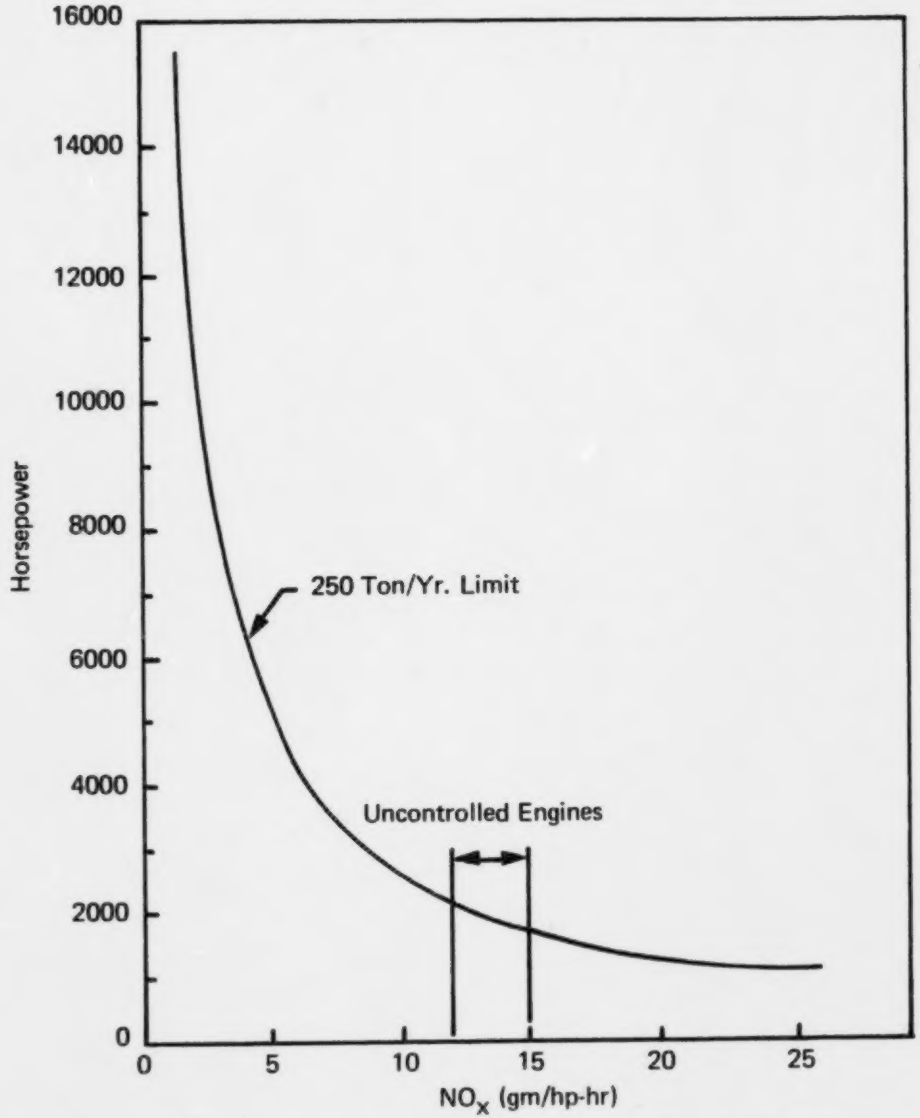

Figure 2. Low NO$_x$ allows larger engine installation without PSD review process.

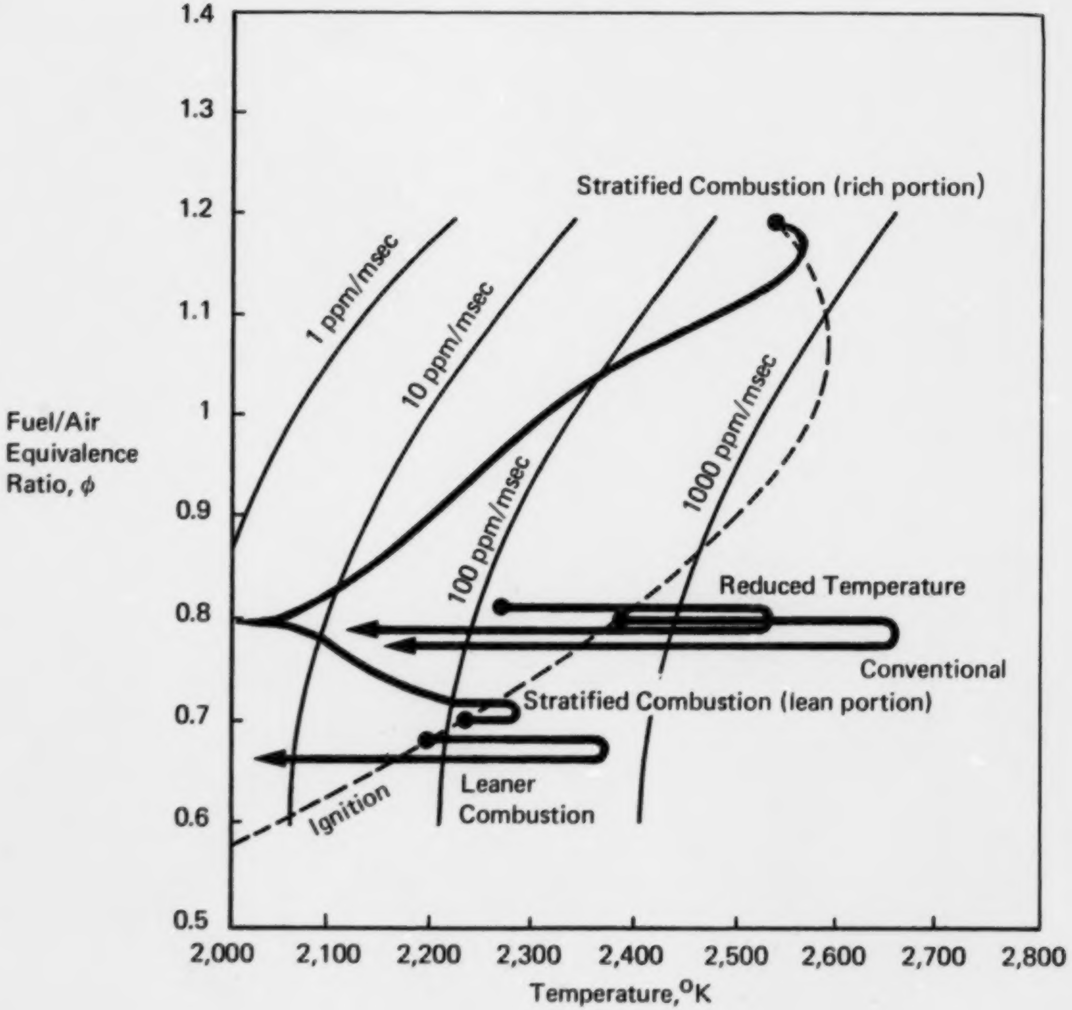

Figure 3. Basic categories of Nitric-Oxide suppression for spark ignition engines.

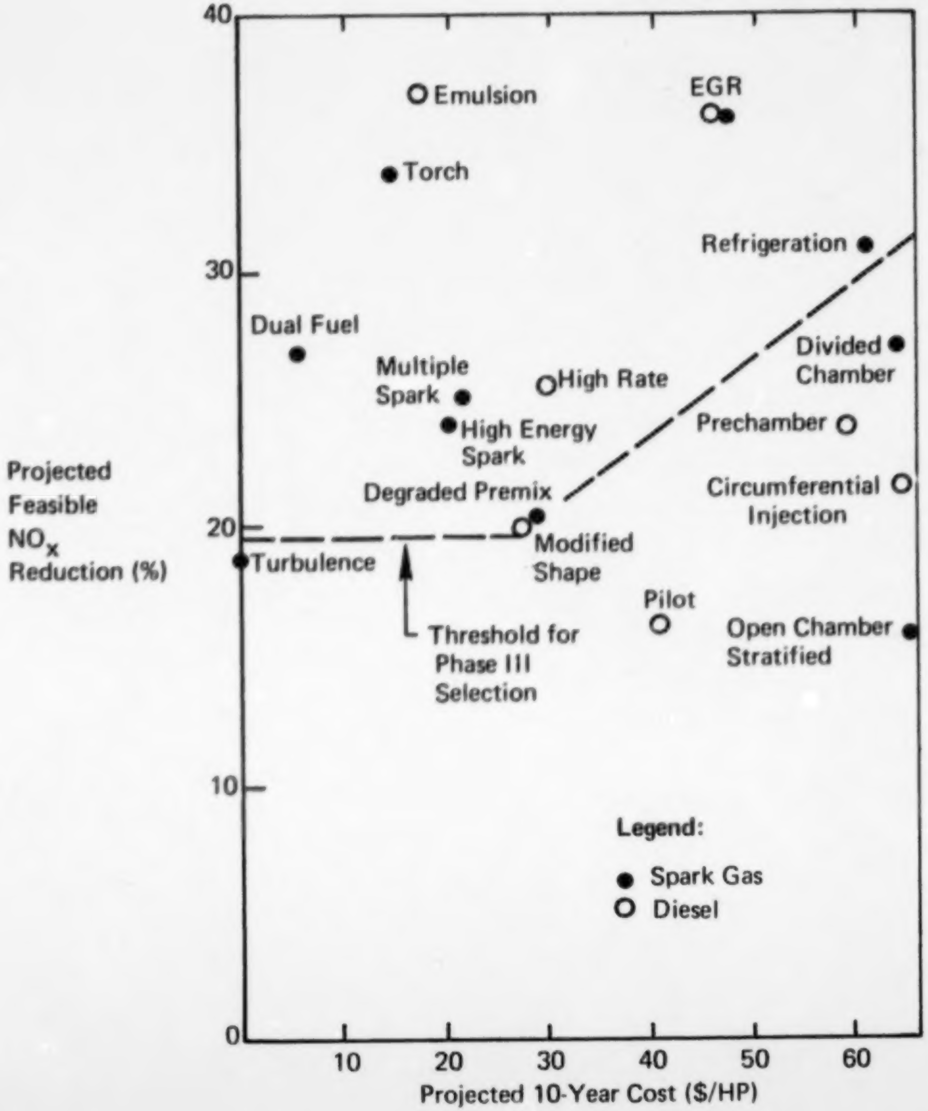

Figure 4. Cost effectiveness of emission control methods

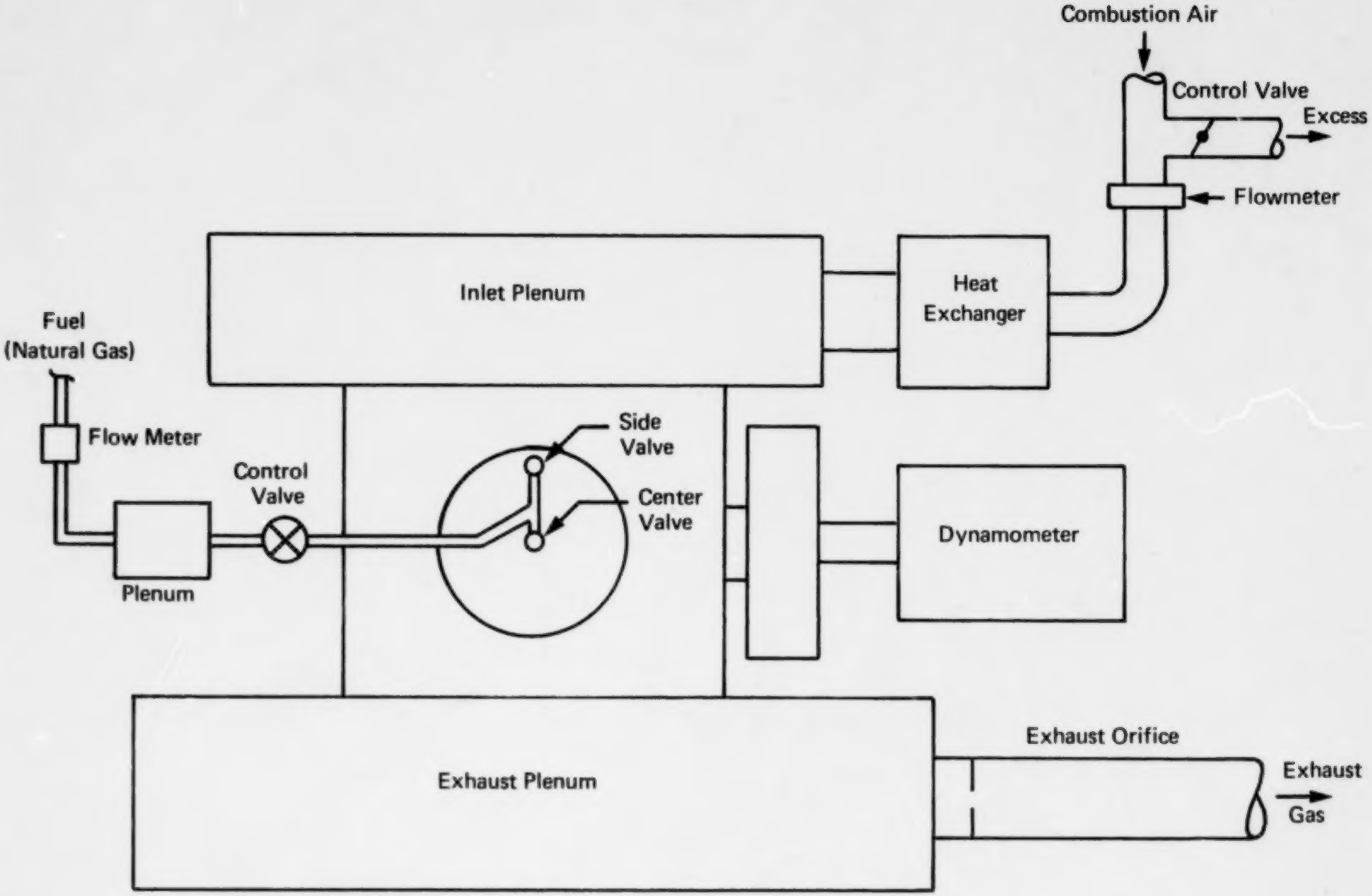
Combustion Air
Control Valve
Excess
Flowmeter
Heat Exchanger
Inlet Plenum
Fuel (Natural Gas)
Flow Meter
Control Valve
Plenum
Side Valve
Center Valve
Dynamometer
Exhaust Orifice
Exhaust Gas
Exhaust Plenum

Figure 5. Plan view schematic laboratory single-cylinder engine Model Z330 (20" bore x 20" stroke).

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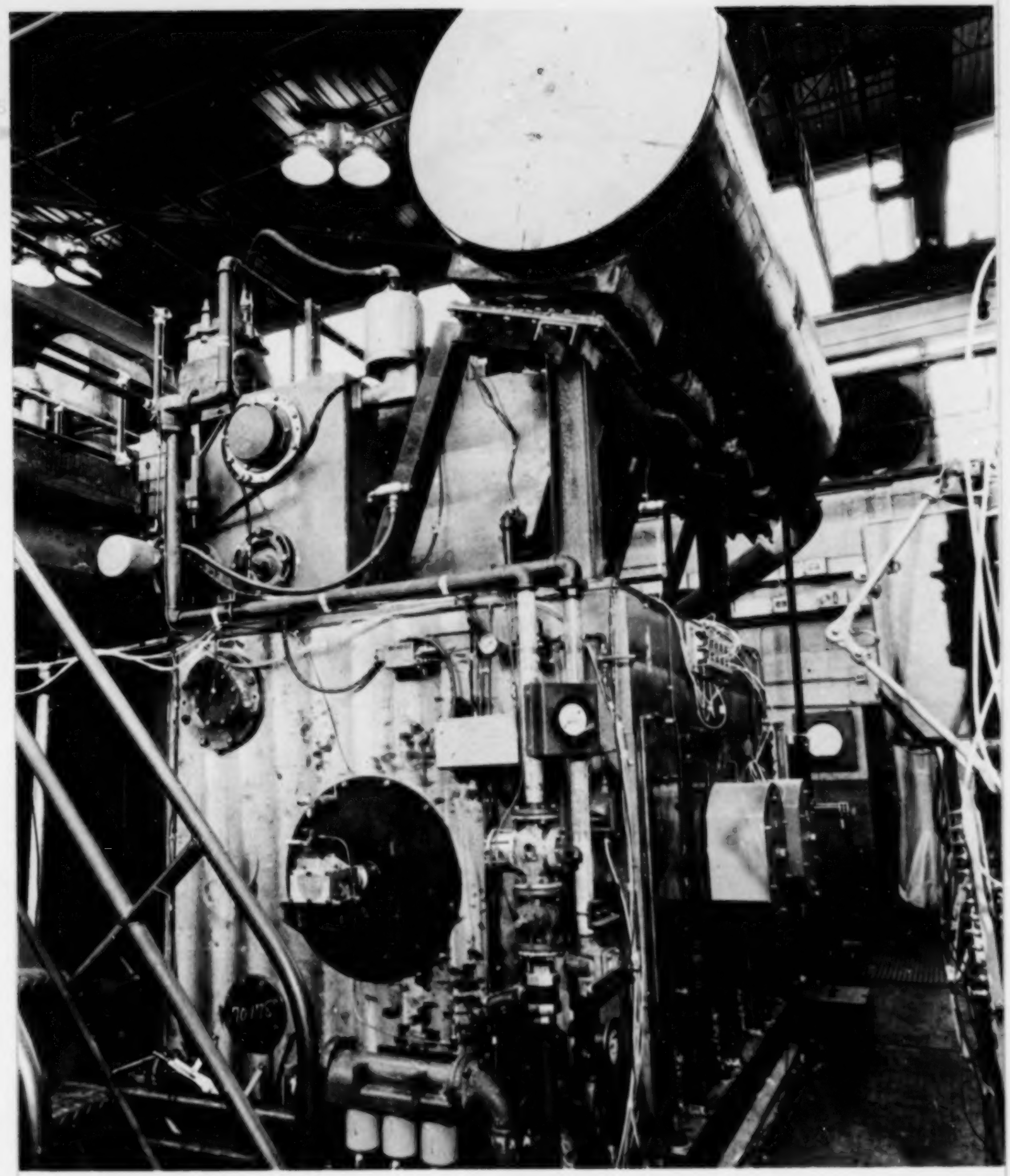

Figure 6. General arrangement of Z330 single cylinder engine.

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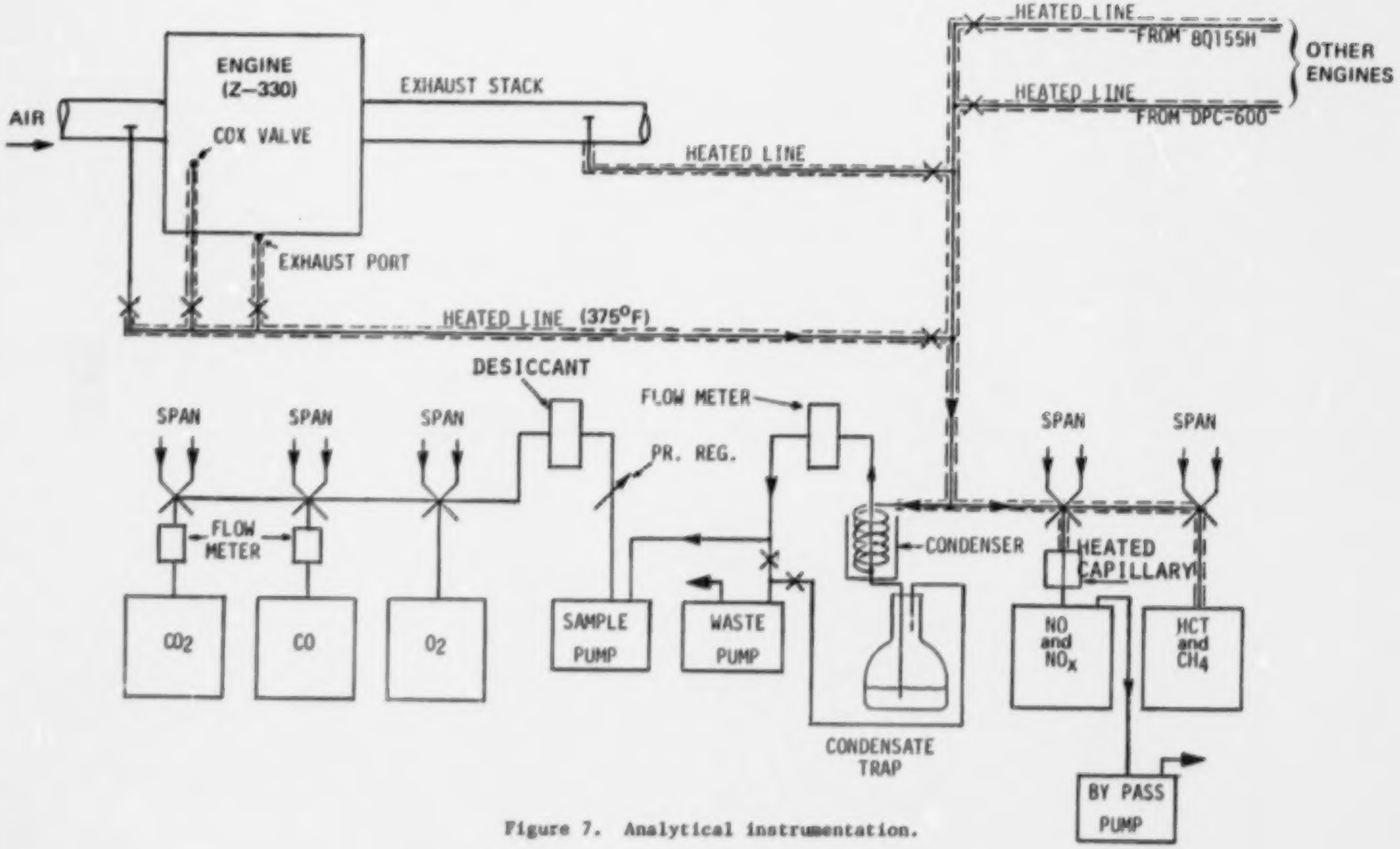
ENGINE (Z–330)
AIR
EXHAUST STACK
COX VALVE
EXHAUST PORT
HEATED LINE
HEATED LINE
FROM 8Q155H
HEATED LINE
FROM DPC-600
OTHER ENGINES
HEATED LINE (375°F)
DESICCANT
FLOW METER
PR. REG.
SPAN
SPAN
SPAN
FLOW METER
CO2
CO
O2
SAMPLE PUMP
WASTE PUMP
CONDENSER
CONDENSATE TRAP
SPAN
SPAN
HEATED CAPILLARY
NO and NOx
HCT and CH4
BY PASS PUMP

Figure 7. Analytical instrumentation.

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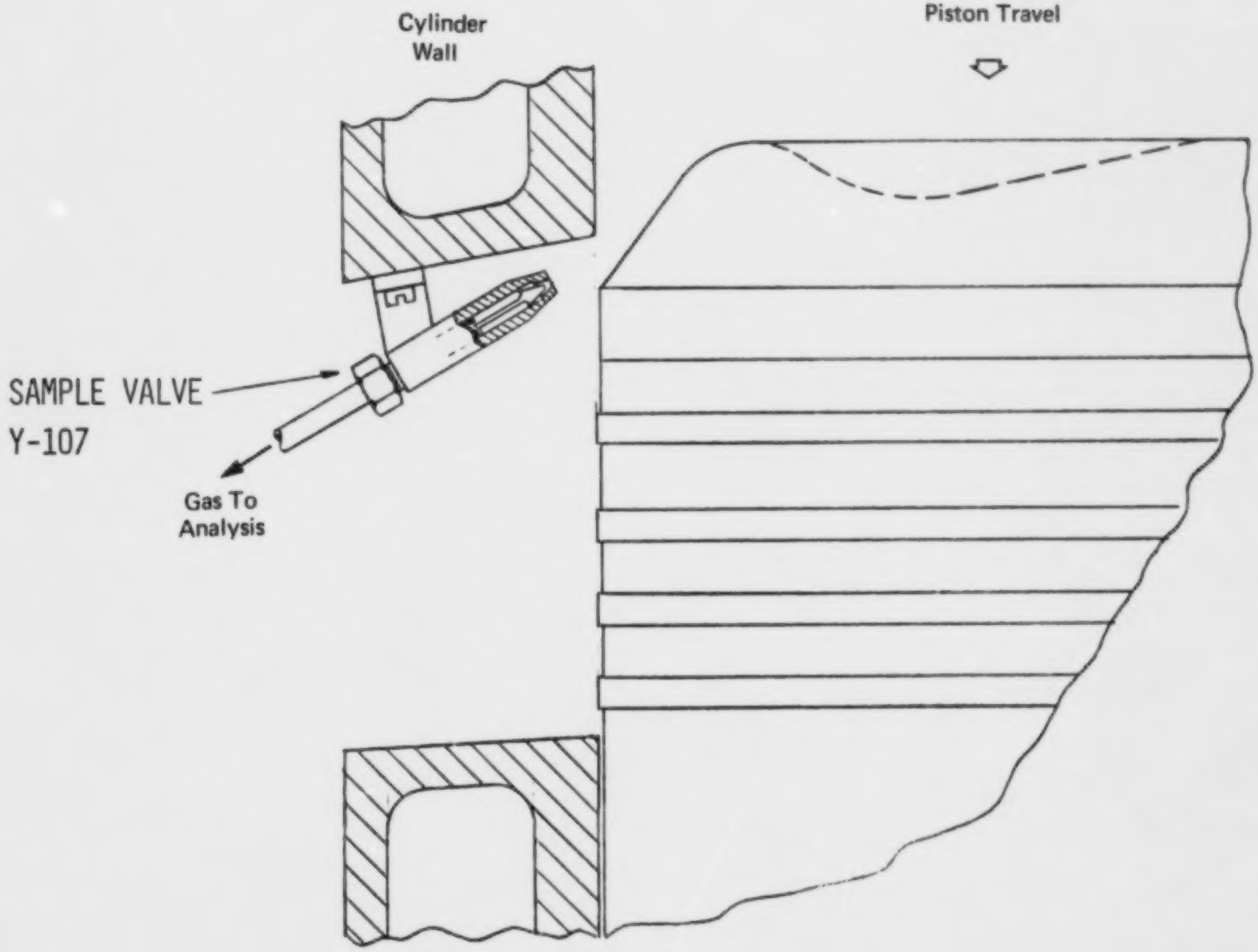
Cylinder Wall
Piston Travel
SAMPLE VALVE
Y-107
Gas To Analysis

Figure 8. Sample valve for extracting cylinder blowdown constituents from exhaust port.

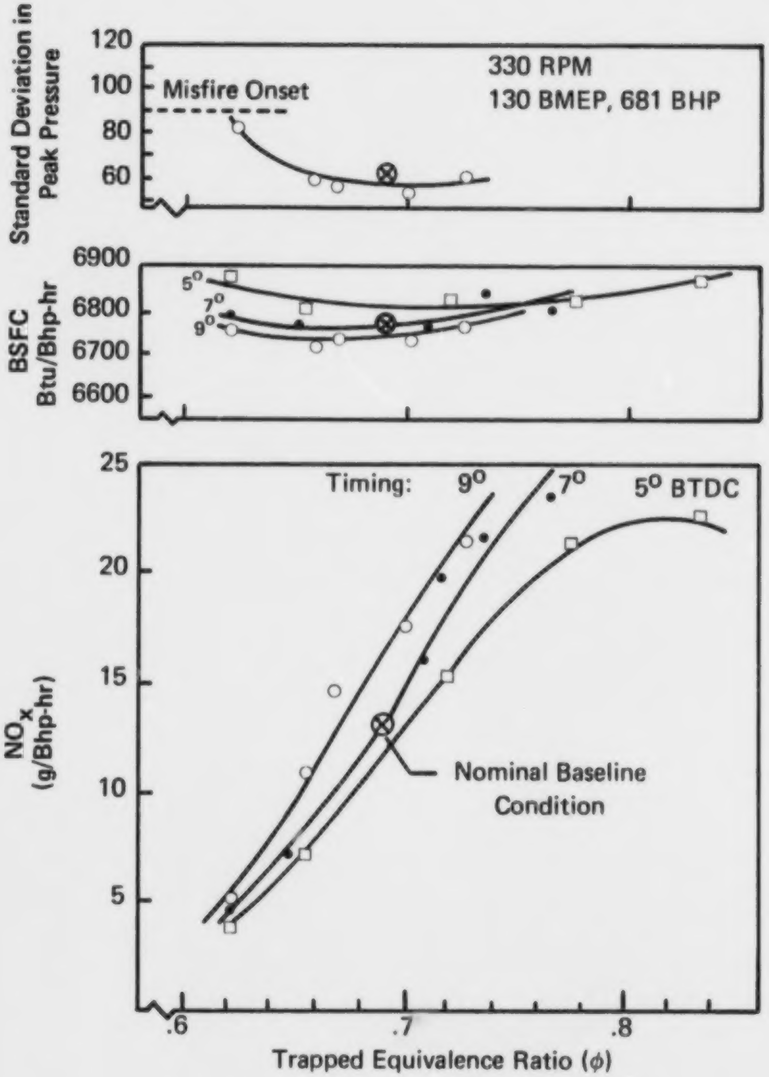

Figure 9. Baseline characteristics Cooper Z330 engine.

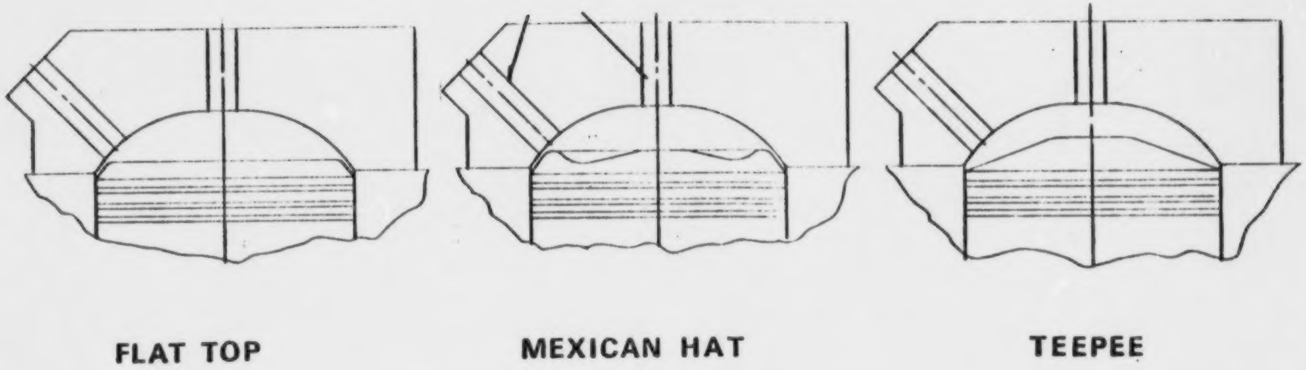
FLAT TOP
MEXICAN HAT
TEEPEE

Figure 10. Piston crown shapes.

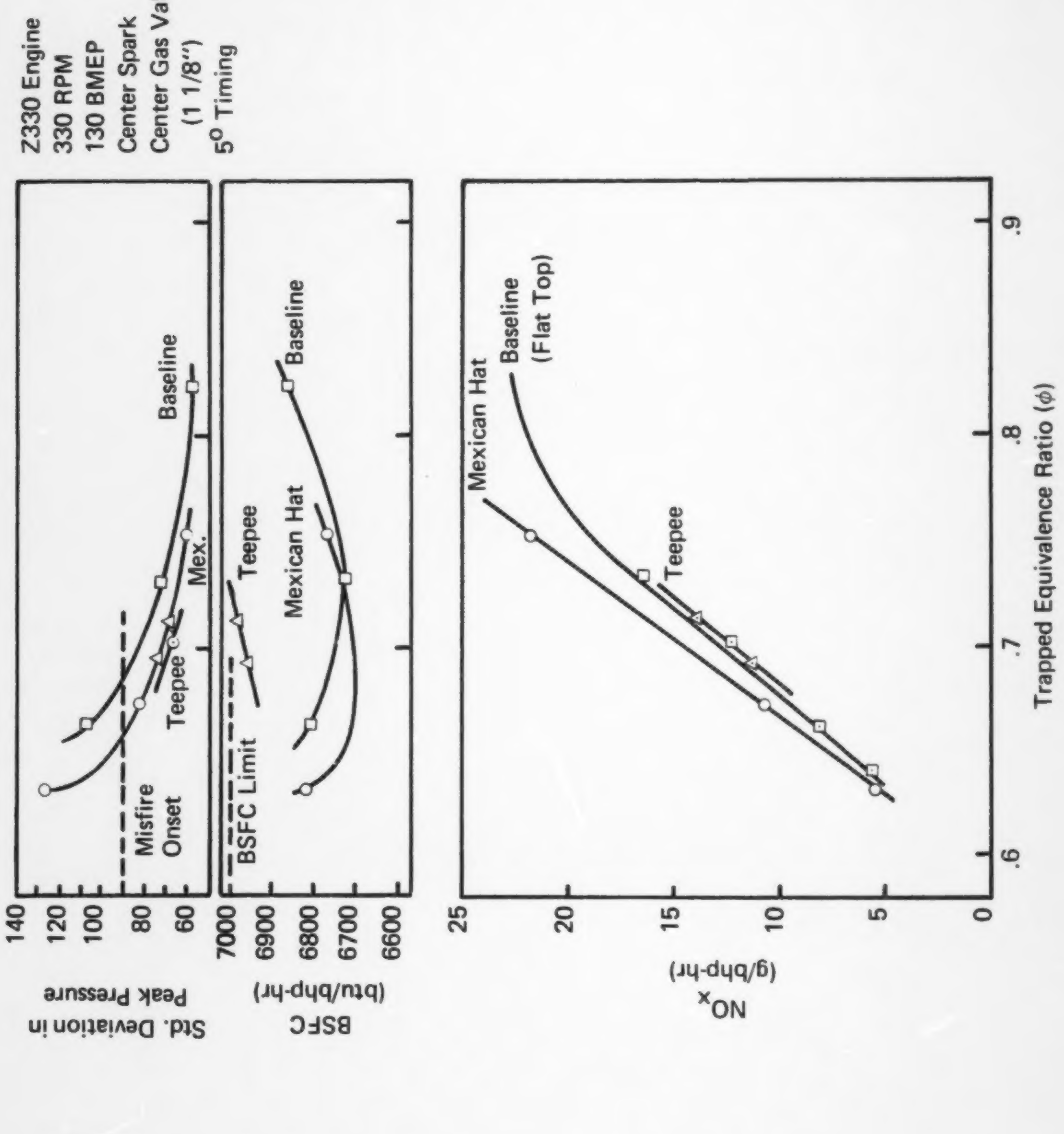

Figure 11. Effect of piston shape.

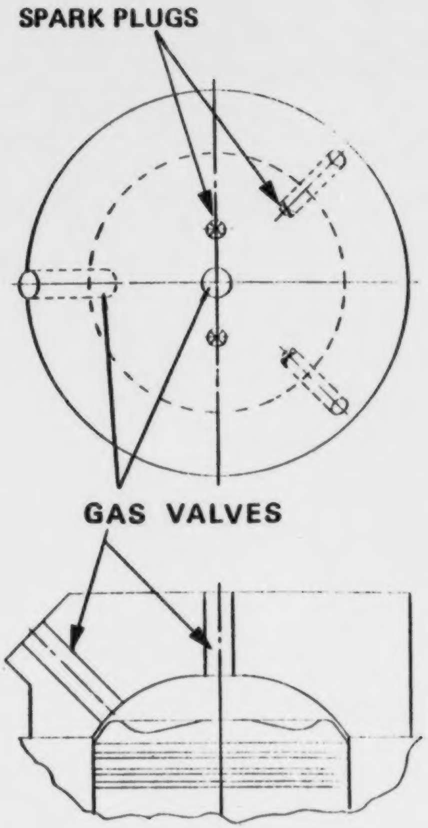
SPARK PLUGS
GAS VALVES

Figure 12. Spark plug and gas valve locations.

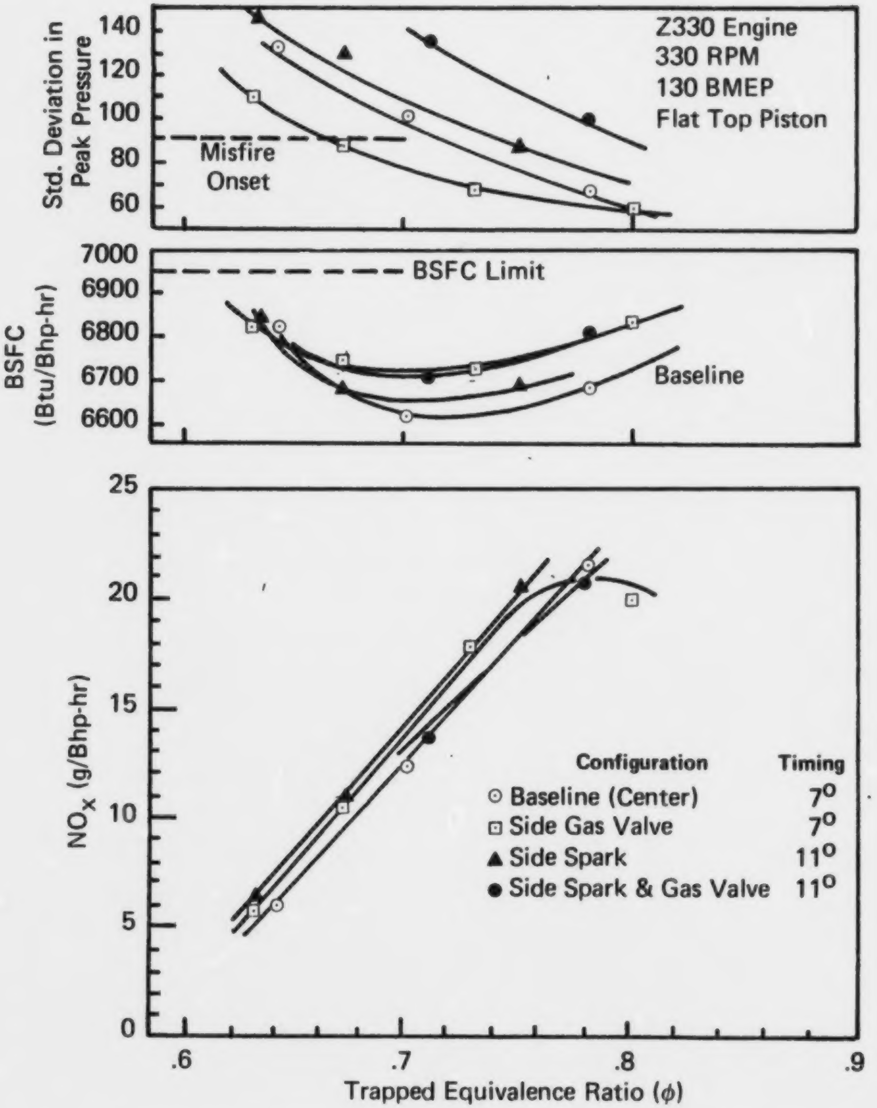

Figure 13. Effect of gas valve and spark location.

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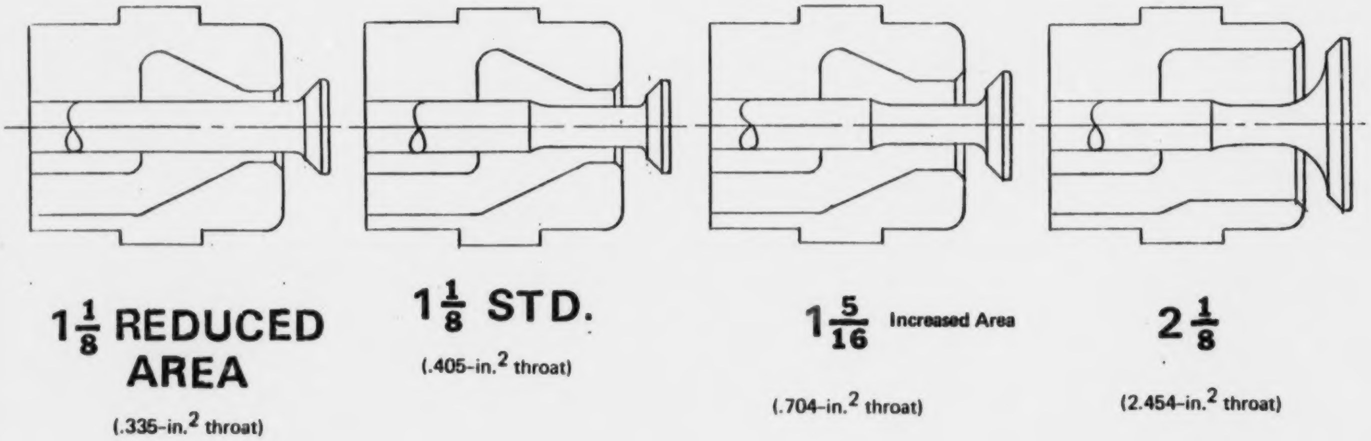
1 1/8 REDUCED AREA
(.335-in.² throat)
1 1/8 STD.
(.405-in.² throat)
1 5/16 Increased Area
(.704-in.² throat)
2 1/8
(2.454-in.² throat)

Figure 14. Gas valves.

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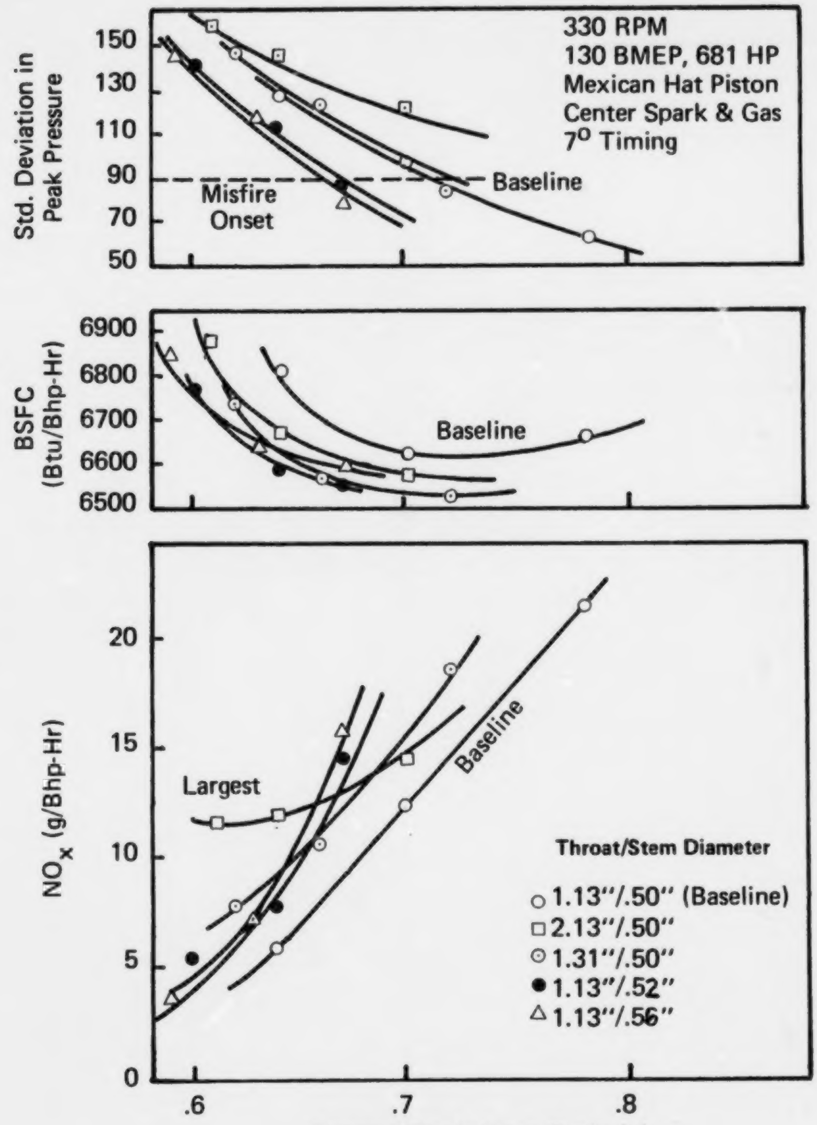

Figure 15. Effect of gas valve modifications.

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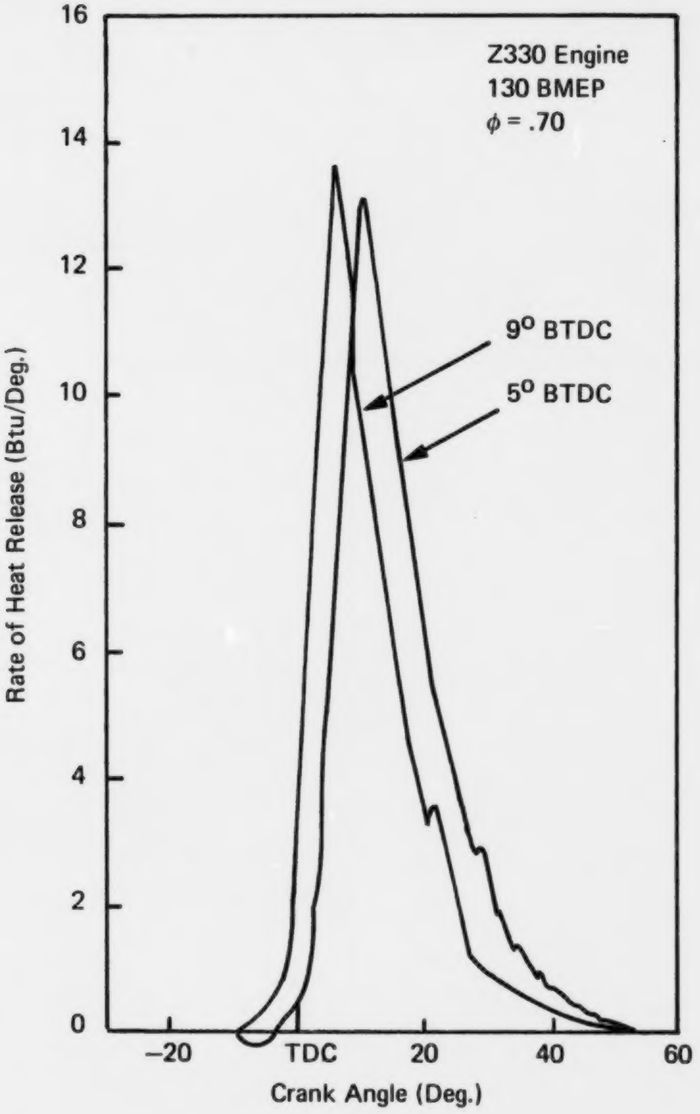

Figure 16. Effect of Timing

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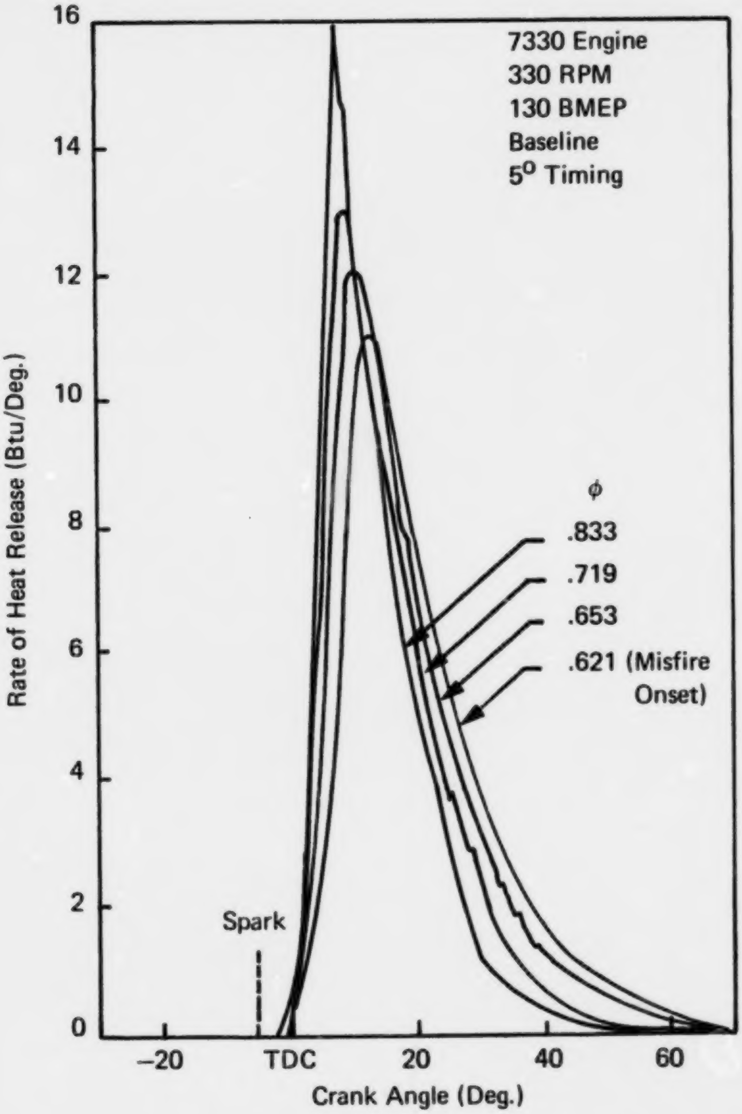

Figure 17. Effect of Fuel-Air Ratio

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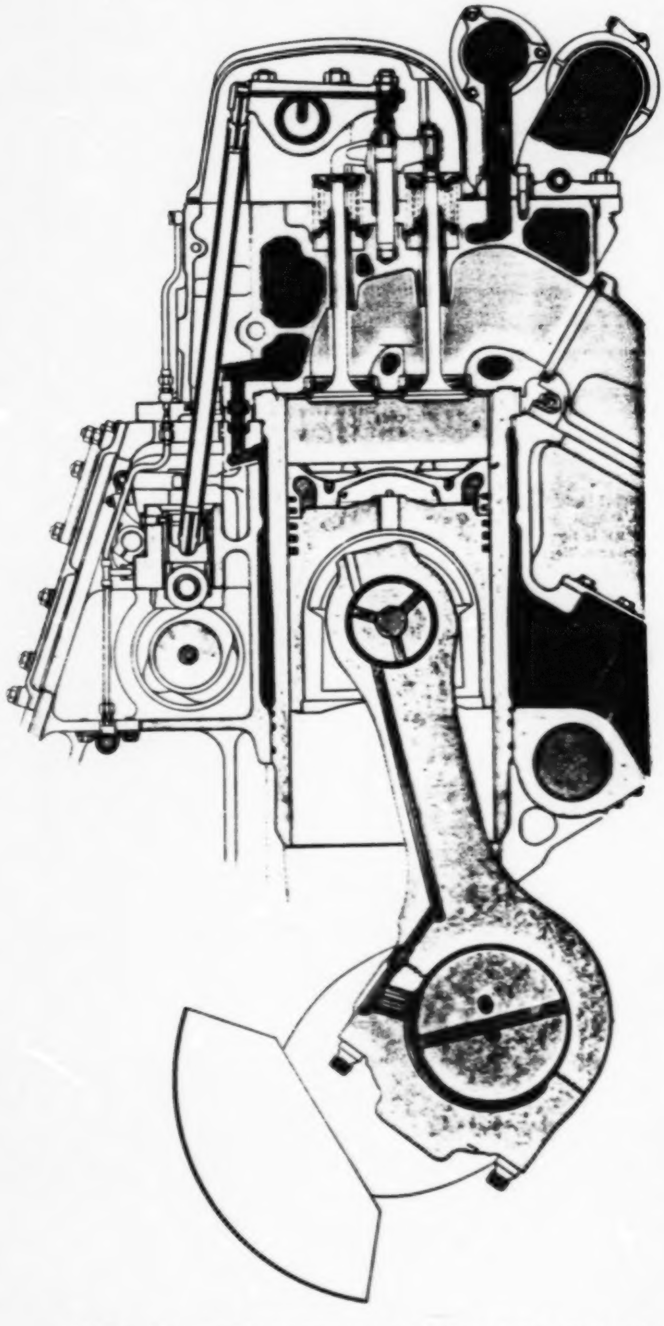

Figure 18. Section across a cylinder of the PA-6 engine

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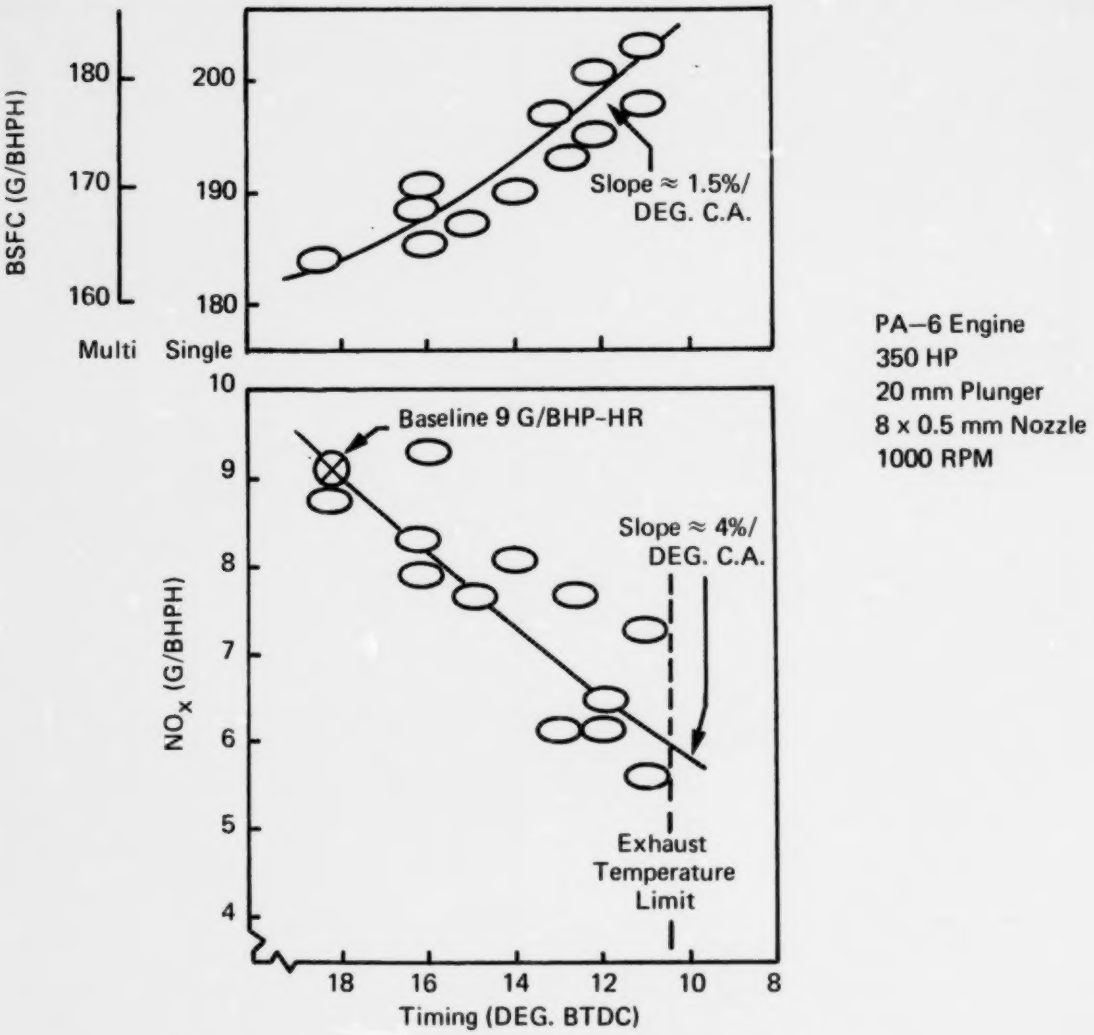

Figure 19. Diesel Baseline Characteristics

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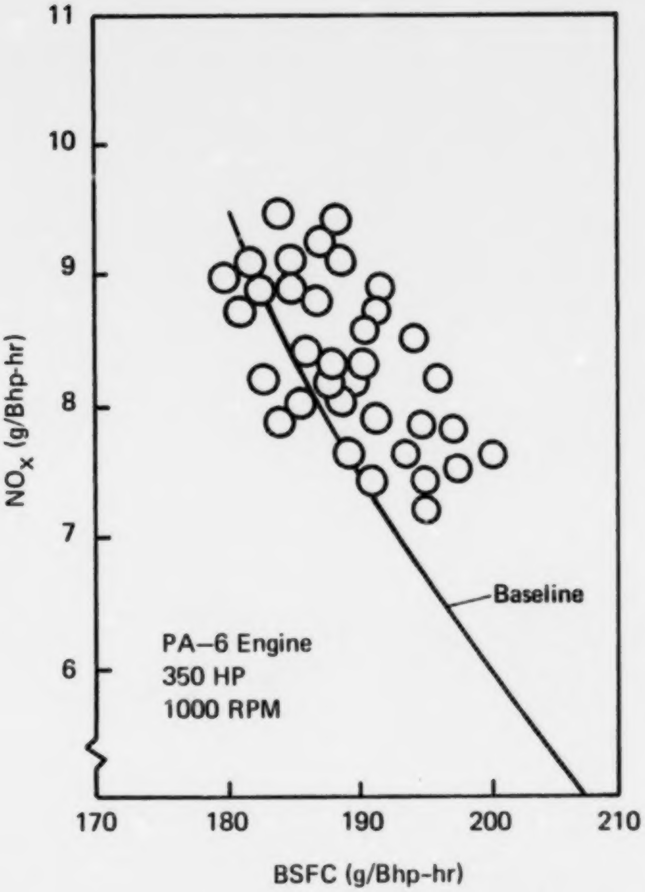

Figure 20. Effect of Pilot Injection (Full Load)

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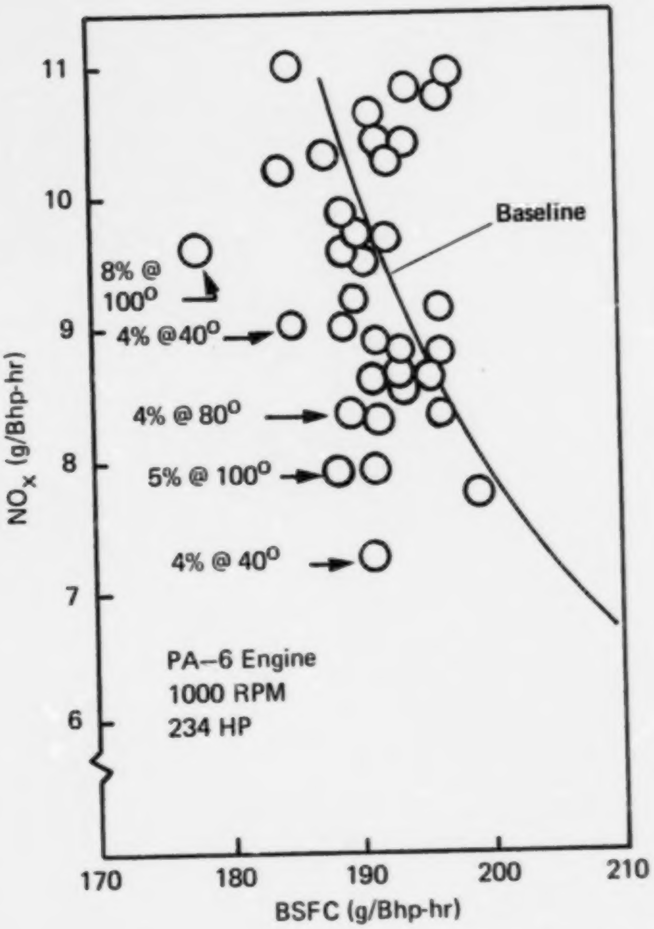

Figure 21. Effect of Pilot Injection (2/3 Load)

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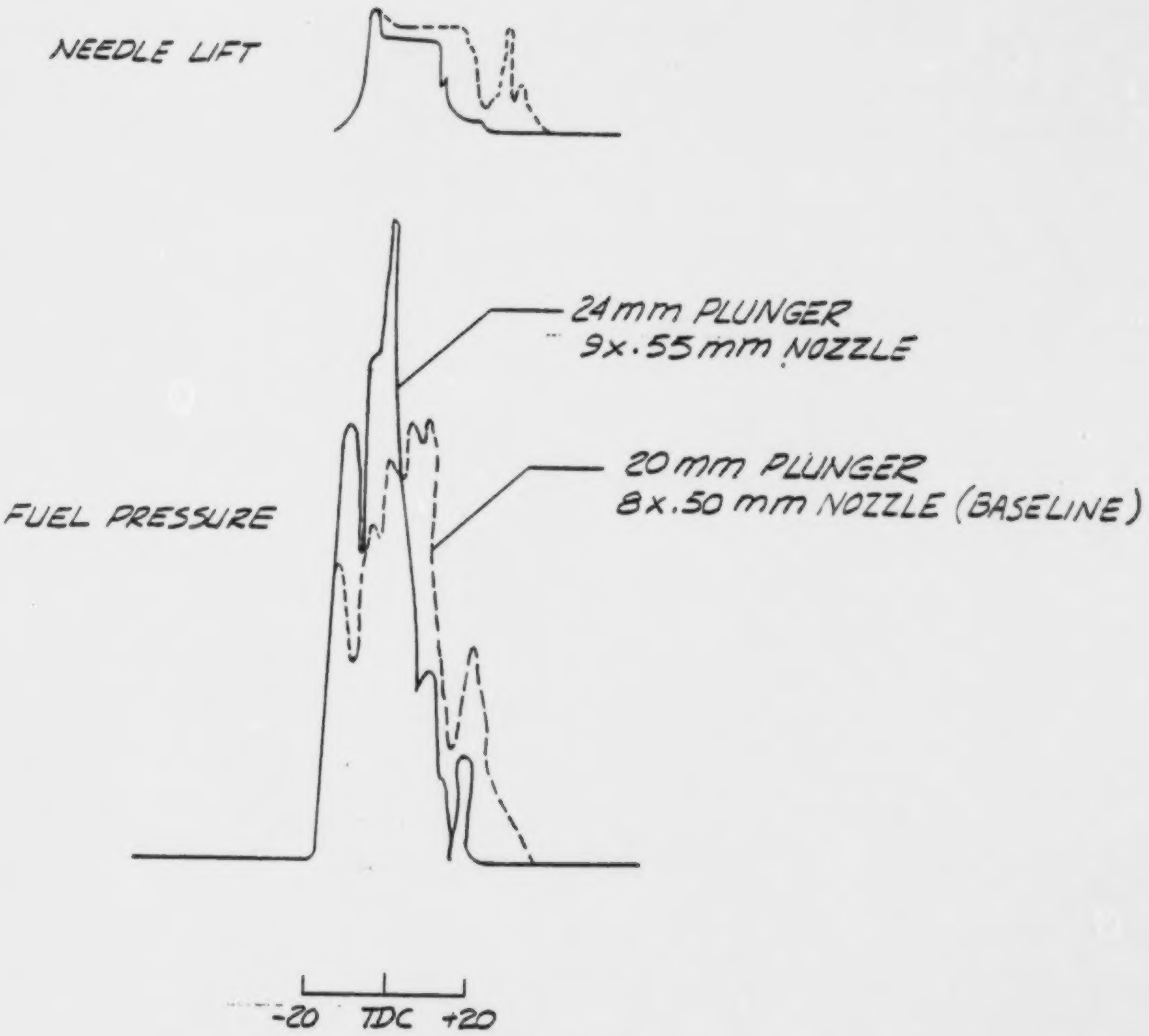

Figure 22. Effect of Plunger/Nozzle on Injection Rate

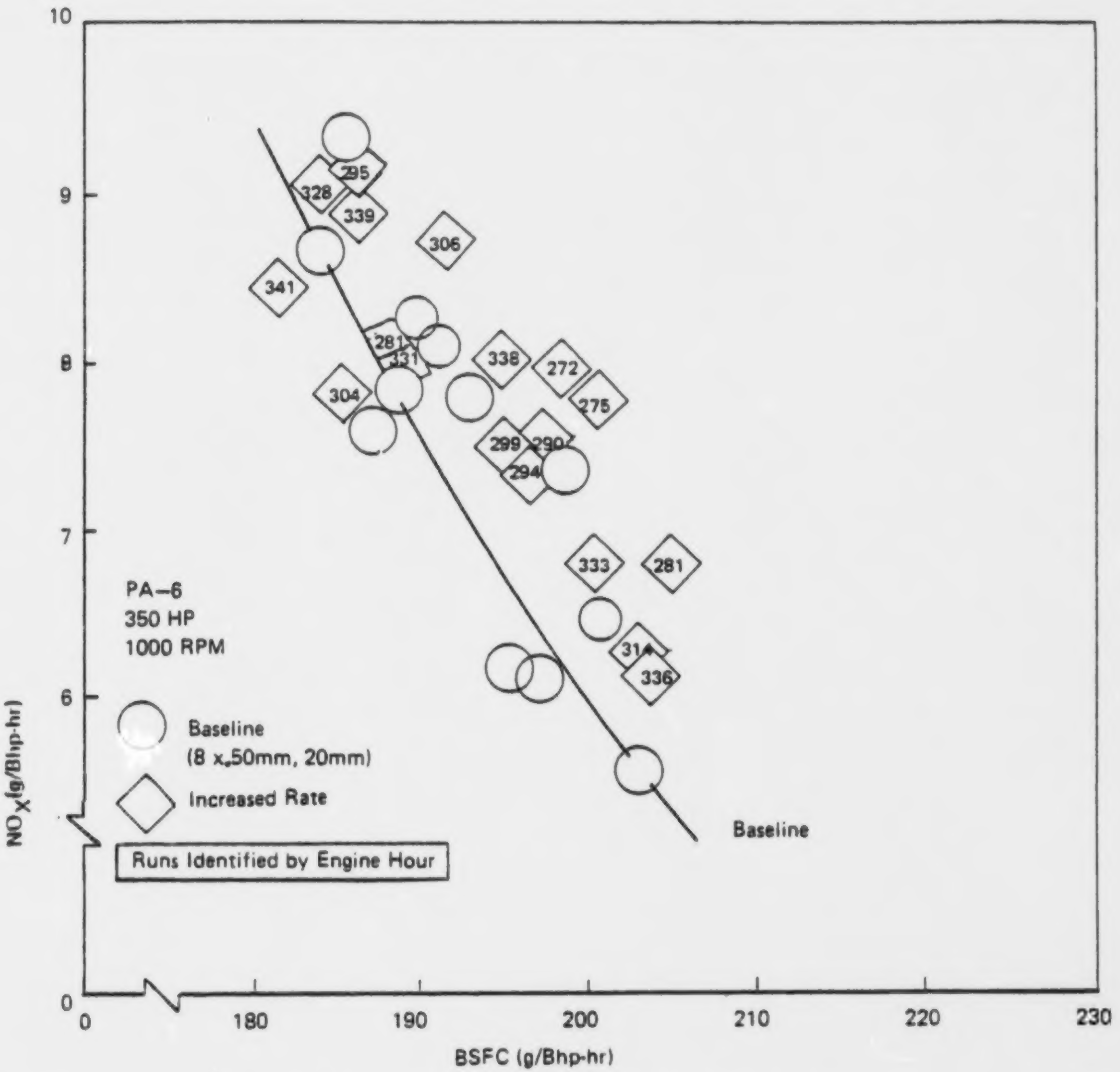

Figure 23. Effect of Rate of Injection

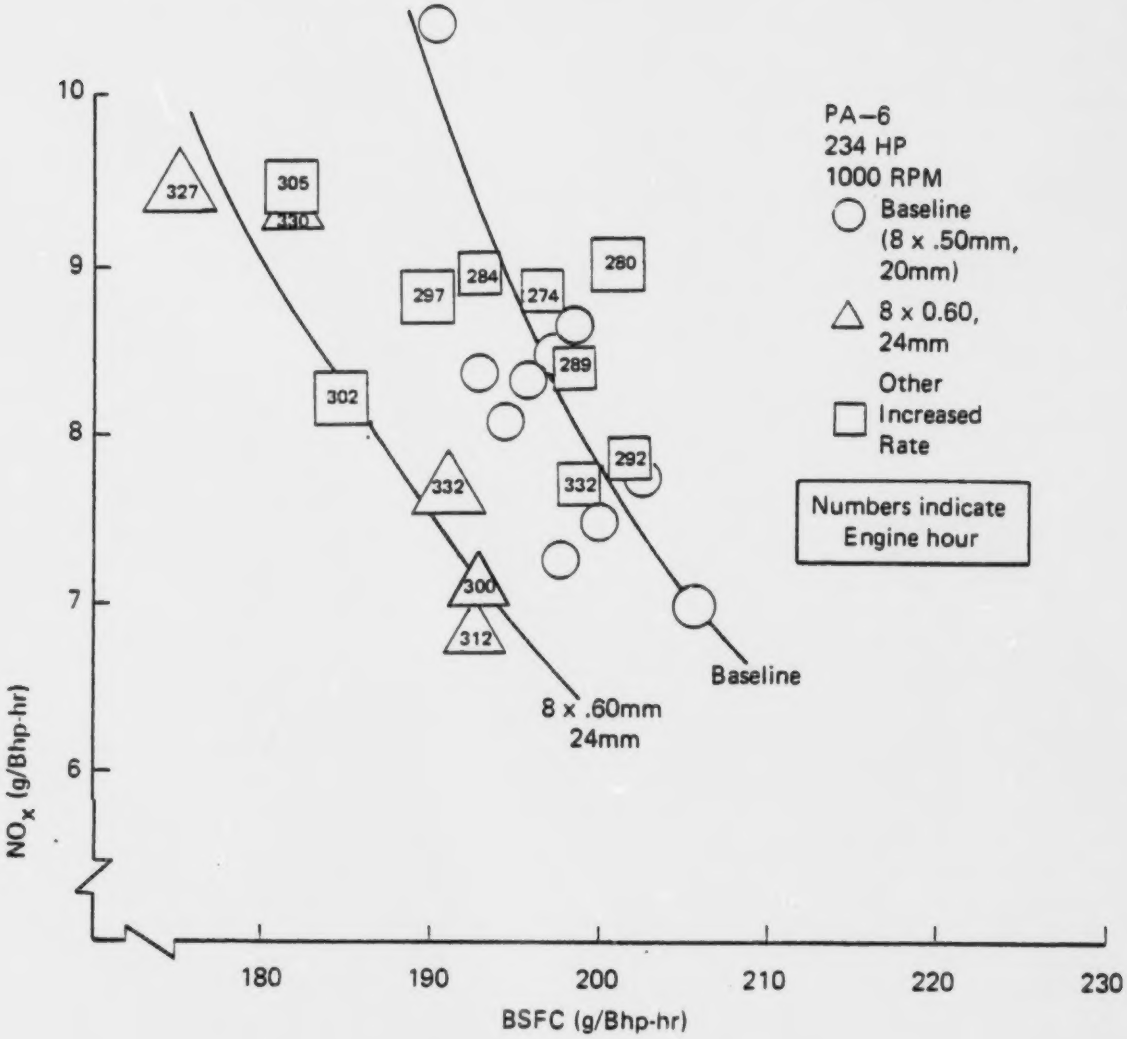

Figure 24. Effect of Rate of Injection

TABLE I: STATIONARY LARGE BORE ENGINE POPULATION

Engine Type	Application	Estimated Annual Fuel Use (10^{14} Btu)
Spark	Gas Pipeline Transmission	3.4
	Gas Gathering, recompression and storage	1.7
Diesel	Deep oil well drilling rigs and oil transport	3.0
	Baseload electricity generators for municipal utilities	1.7
	Standby generating sets for nuclear and hospitals	0.7
	Industrial power and water/sewage pumping	0.6
	TOTAL	11.0
		(1.5% of U. S. Fuel Use)

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TABLE II: NO_x EMISSION RATE OF LARGE BORE ENGINES COMPARED TO OTHER COMBUSTION DEVICES

Device	Typical NO_x Emission (lb/MM Btu)
Large Bore Engines	4.0
Automotive SI Engines	2.0
Coal Fired Utility Boilers	0.7
Industrial & Commercial Boilers (Oil Fired)	0.4
Industrial Furnaces (Gas Fired)	0.3
Residential Furance and Water Heater	0.1

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TABLE III: MAJOR PHASES OF WORK

		Share of Project Resources
PHASE I (4 months)	Identify emission-control methods (34 identified)	3%
PHASE II (11 months)	Evaluate the methods to select the 12 most promising based on: ● predicted NO_x reduction ● retrofit feasibility ● BSFC effect ● cost	14%
PHASE III (24 months)	Operate single-cylinder 20"-bore spark and 11"-bore diesel engines to test the 12 promising emission control methods	66%
PHASE IV (9 months)	Field tests on multicylinder engines	17%

TABLE IV: PHASE III TESTING

SPARK IGNITION	Conventional	Spark Location Gas Valve Location Piston Shape
	Lean Burn	Multiple Spark Torch Ignition High Energy Spark Feedback Control
	Stratified Charge	Degraded Premix
	External	Charge Refrigeration NH_3/Catalyst
DIESEL	Retarded Timing	Emulsion High Injection Rate Pilot Injection
	External	EGR NH_3/Catalyst

TABLE V: FUEL COMPOSITION (NATURAL GAS)

	March 1979	July 1979	October 1979	January 1980
Methane	95.70%	96.00%	97.96%	95.07%
Ethane	3.20	3.00	1.07	1.82
Propane	.17	.14	.21	.27
Butanes	.03	.04	.08	.12
C_5 and up	.03	.04	.06	.08
Nitrigen	.35	.37	.20	2.18
Carbon Dioxide	.47	.40	.42	.45
Heating Value $(Btu/scf)_{dry}$	1016	1033	1024	1011

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TABLE VI: TEST MATRIX FOR CONVENTIONAL TECHNIQUES

	CENTER SPARK		SIDE SPARK	
	Center Gas	Side Gas	Center Gas	Side Gas
Timing	9 7 5 3°	9 7 5 3°	13 11 9 7°	13 11 9 7°
Mexican Hat Piston	- ● ● -	- ● ● ●	- ● ● -	- ● ● -
Teepee Piston	● ● ● ●	● ● ● -	● ● - -	● ● ● -
Flat Top Piston	- ● ● -	- ● ● -	- ● ● -	- ● ● ●

Each dot represents 3 to 5 runs, varying F/A.

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TABLE VII

PRELIMINARY DATA ON LEAN-BURN ENGINES

Source	Engine	Configuration	NO_x (g/bhp-hr)	Fuel Penalty
Cooper Bessemer (EPA Program)	Z330 20" Bore 1-Cylinder	Increased Air Pressure* (ϕ = .72 → .62)	16.2 → 4.9 (70%)	1–2%
Cooper Bessemer (Helmich, 1979)	GMVH 14" Bore 12-Cylinder	● Jet-Cell ● Modified TC ● Retarded Timing	10.2 → 3.0 (70%)	2.6%
Cooper Superior (Chrisman, 1980)	SGT 10" Bore 2-Cylinder	● Pre-Chamber ● Retarded Timing ● ϕ = .67 → .54	13.0 → 4.0 (70%)	Unspec.

*No Turbocharger Limitation

TABLE VIII: INJECTION SYSTEMS TESTED

Plunger size	Number of holes	Hole size
20 mm	8	.50 mm
22 mm	8	.50 mm
	8	.55 mm
	9	.50 mm
	10	.48 mm
24 mm	8	.60 mm
	9	.55 mm
	10	.55 mm

EMISSION REDUCTION BY COMBUSTION MODIFICATION FOR PETROLEUM PROCESS HEATERS

By:

R. J. Tidona, W. A. Carter,
J. R. Hart and S. C. Hunter
KVB, Inc.
Irvine, California 92714

Emissions Reduction by Combustion Modification for Petroleum Process Heaters

R. J. Tidona, W. A. Carter and S. C. Hunter
KVB, Inc.

ABSTRACT

This paper is based upon work sponsored by EPA to evaluate combustion modification technology applied to industrial process equipment. The test program described herein was aimed at the development of combustion modifications for reducing NO_x emissions from process heaters. In particular, staged combustion air and lowered excess air were applied separately and in combination to a natural draft vertical cylindrical crude heater and the effects on heater efficiency and NO_x emissions were studied.

At a crude throughput of approximately 59 percent of the heater capacity, reductions in NO_x emissions of over 50 percent from baseline emission levels were observed when firing refinery gas fuel and using the combined modifications of staged combustion air and lowered excess air. Burner and heater performance actually improved slightly with the application of these modifications. An increase in heater efficiency of over two percent was observed for low-NO_x-firing as compared to baseline conditions.

The same modifications were tried firing residual oil simultaneously with the gas fuel. Some reduction in NO_x emission was achieved, however the magnitude of the reduction was smaller than that obtained for gas fuel only.

The cost effectiveness in dollars per unit mass of NO_x removed is calculated and the feasibility of the staged air/low excess air modification for retrofit application to natural draft process heaters is discussed.

SECTION 1

INTRODUCTION

At the Third EPA Stationary Source Combustion Symposium, KVB reported on subscale process heater combustion modification tests. The report summarized the effects on NO_x emissions of several types of modifications, including staged combustion air, flue gas recirculation, lowered excess air, altered injection geometry, and low NO_x burner installation. The work showed that staged combustion air appears to be the most cost effective combustion modification for process heaters. Both staged air and flue gas recirculation produced NO_x emission reductions in excess of 60 percent below baseline emission levels.

COMBUSTION MODIFICATIONS TO A FULL SCALE PROCESS HEATER

The present report summarizes the testing of a full scale natural draft refinery process heater firing natural gas, refinery gas, and No. 6 oil fuels. A staged air injection system was designed by KVB and installed by the refinery for these tests. The system is capable of supplying up to 50 percent of the stoichiometric air requirement. The staged air is injected by means of lances inserted through the heater floor as it was in one of the subscale test configurations. The process heater was tested with and without the staged air modification and over a range of loads and stack excess oxygen concentrations. Stack gas emissions and heater efficiencies were measured for all conditions.

Lowered excess air and staged combustion air modifications were applied separately and in combination. NO_x emission reductions of up to 52 percent below baseline levels were achieved when firing gas fuel with no short term ill effects on the heater. Heater efficiency was increased at the low NO_x conditions due to the lowering of excess air. Staging the combustion air did not appear to significantly alter efficiency; the same level of lowered excess air was attainable both with and without staging.

In the most favorable situations the combination of staged air and lowered excess air costs \$64/Mg NO_x reduction. Staged combustion air applied separately is expected to be considerably more expensive-approximately \$2600-\$3000 per Mg NO_x reduction.

OBJECTIVE AND SCOPE

The objective of the program is to develop advanced combustion modification concepts requiring minor hardware modifications that could be used by operators and/or manufacturers of selected industrial process equipment to control emissions. The development is aimed at equipment on which the modifications will be most widely applicable and of the most significance in mitigating the impact of stationary source emissions on the environment. The program involves investigation not only of emissions but also multimedia impacts and control cost effectiveness.

The program includes both subscale and full-scale testing. Subscale testing is a necessary part of development of new hardware to ensure acceptable performance, which is a vital aspect of emissions control. Full-scale testing is also necessary on more than one process design configuration (e.g., forced draft and natural draft) before equipment manufacturers and the process industry can employ a given emission control technology.

At the conclusion of the study, a final engineering report will be prepared summarizing the accomplishments of the subscale and full-scale demonstration tests. A series of guideline manuals will be prepared to acquaint equipment manufacturers with the most promising emission control methods that have been demonstrated and to offer technical guidance that can be directly applied in their process equipment design.

SECTION 2

TEST HEATER AND EMISSIONS SAMPLING

TEST UNIT DESCRIPTION

The test unit was a natural draft, vertical cylindrical crude oil process heater which is used to supply a partially vaporized charge to a crude oil distillation column. A maximum load of 108 m^3/h (16,250 bbl/d) may be sent through the heater in two passes. A sketch of this crude oil heater is presented in Figure 1.

The maximum firing rate of the heater is 16.1 Mw thermal input (55 x 10^6 Btu/hr). It is fired by six John Zink DBA-22* natural draft burners. The burners are combination gas/oil burners rated at a maximum of 2.68 Mw (9.14 x 10^6 Btu/hr) each with a turndown ratio of 3:1. Although combination gas/oil burners are used, some gas must always be fired because the unit is base loaded at constant oil firing rate and an automatic temperature controller adjusts the gas fuel flow to maintain crude oil outlet temperature.

Three parameters may be controlled in the heater: excess oxygen, (by furnace draft), firing rate, and load. The stack damper is the main control for the pressure drop across the furnace. The pressure drop may also be controlled by opening or closing the secondary air registers which are in the base of the heater. Each burner has a set of primary and secondary registers which can be adjusted independently of the other burners. The stack damper and register adjustments establish the excess oxygen. The load is controlled by pumps and valves on the inlet and outlet of the heater.

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*Mention of trade names does not constitute endorsement by the Environmental Protection Agency.

STAGED AIR SYSTEM DESCRIPTION

This application of staged combustion utilizes air lances in the firebox to supply air to the flame zone a given distance above the base of the flame. Figure 2 presents a schematic of this system.

The system consists of twenty-four vertical 316 stainless steel pipes 3.18 cm (1-1/4 in.) diameter arranged four per burner at 90° apart. A 45° elbow is placed on each pipe to provide better mixing across the flame. A fan supplies air to the lances through a manifold and flexible tubing. The lances may be varied in height up to 1.2 m (four feet) from the base of the burners. Extensions for the lances allowed staging heights up to 2.4 m (eight feet) for oil firing tests.

EMISSIONS SAMPLING INSTRUMENTATION

Monitoring of the required gaseous and particulate emissions was performed with an EPA furnished mobile laboratory. The laboratory's monitoring capabilities are presented in Table 1. A schematic of the continuous monitoring system is presented in Figure 3. A detailed description of a similar mobile emissions laboratory has been presented in a previous report (Ref. 1).

Continuous gaseous emissions analyzers provide the capability for measurement of O_2, CO_2, CO, SO_2, NO, NO_x, and HC (as methane) in the flue gas. Particulate total mass and sizing as well as SO_3 measurements are non-continuous. SO_3 measurement is by a controlled condensation technique using a Goksoyr-Ross type coil.

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1. Hunter, S.C., et al. "Application of Combustion Modifications to Industrial Combustion Equipment," EPA Report 600/7-79-015a, NTIS Order No. PB 294214, January, 1979.

The O_2, CO_2, and CO concentrations are measured on a dry basis. SO_2, HC, and NO_2 measurements are made through a heat-traced sample line and are determined on a wet basis. NO may be sampled either wet or dry.

SECTION 3

DISCUSSION OF RESULTS

LOAD AND EXCESS OXYGEN VARIATIONS

A series of tests was conducted to evaluate the performance of the process heater with regard to NO_x emission and efficiency over varying load and excess oxygen conditions. These tests were first made while firing a gaseous fuel mixture consisting of natural gas and refinery fuel gas and then while firing residual oil simultaneously with the gas mixture.

The NO emissions as a function of excess oxygen are shown in Figures 4 and 5. The highest NO emission generally occurred at the intermediate load condition, 70% of rated capacity. NO_x emission increased with increasing excess oxygen up to approximately 4-6 percent O_2 for all fuel combinations. In the 4-6 percent O_2 range, NO emission was relatively insensitive to excess O_2 level and, at higher excess O_2, NO emissions decreased.

The nitrogen content of the gaseous fuels was negligible whereas the nitrogen content of the oil fuel was 0.8 percent by weight, hence, the difference in absolute NO emission between Figures 4 and 5. Several ratios of oil/gas are reported in Figure 5. These ratios indicate the approximate fuel split by percentage of total heat input. Changes in the fuel split occurred because a) gas fuel composition and heating value could change in a short time period and b) total heat input required to maintain the load could change due to changes in the composition of the crude charge to the heater.

At the intermediate load, the baseline excess oxygen was 4 percent which was regarded by the plant as a normal operating level. The excess oxygen variation tests indicated that continuous operation of the heater at 2 percent excess O_2 was possible without additional operator supervision. Below this level the heater draft tended to become unstable. Fluctuations in the draft caused occasional smoking of the unit and resulted in positive stack or convection section pressures which are dangerous in a natural draft heater because they can cause flashback. Flashback occurs when a flame encounters a back pressure which forces it downward and out the bottom of the heater through the air registers.

STAGED COMBUSTION AIR TESTING

The next phase of testing at the process heater site involved the evaluation of the staged combustion air system. This evaluation included the variation of three important parameters: 1) burner equivalence ratio, Φ_B, 2) excess oxygen level, and 3) staged air insertion height.

For the staged combustion air tests, due to changes in plant operation, it was necessary to fire a different refinery gas from that used in load and excess oxygen variations. This gas, called "adsorber gas," contained a greater percentage of higher hydrocarbons than did the "fuel gas" or natural gas and, therefore, a higher heating value. Baseline NO emission with adsorber gas was about 8 percent higher (8 ppm) compared with fuel gas.

The NO emission is graphed as a function of burner equivalence ratio, $\phi_B = \frac{(A/F)_{\text{Burner}}}{(A/F)_{\text{Stoichiometric}}}$. The staging height for this test series was 1.2 m (4 ft.) and the load was $64 m^3/h$ (9600 bbl/d), 60 percent of rated capacity. At each overall excess O_2 level Φ_B was decreased in steps to its minimum value which was determined by the limitations of the staged combustion air fan. Figure 6 shows that at 4 percent O_2 the minimum Φ_B (maximum staging) obtained was 0.74 which decreased NO emissions 35 percent below the baseline of 105 ppm, dry at 3 percent O_2. At 2 percent O_2 and minimum Φ_B of 0.65 the NO concentration dropped to 51 ppm, dry, corrected to 3 percent O_2. This represented a reduction of 51 percent below the 4 percent O_2 baseline condition and a 43 percent below the 2 percent O_2 (non-staged) level. Table 2 summarizes the NO_x

reductions and efficiency changes for the various combustion modifications to the process heater while firing adsorber gas.

Figure 7 shows similar trends in NO emissions for varying Φ_B and excess O_2 at a higher load. The same degree of staging could not be achieved at the intermediate load because of fan capacity limitations, however, the curves in Figure 7 indicate that roughly the same NO_x reductions would have been obtained had the minimum Φ_B values of Figure 6 been reached.

The results of another test series in which overall excess oxygen and burner equivalence ratio were kept constant while varying staged air insertion height are shown in Figure 8. (The staged air height is defined as the height above the heater floor at which the staged combustion air is injected. This is approximately equal to the height above the burner gas tips and oil gun.) There was little, if any, effect of staging height on NO emissions. Since the burner tile top was about 0.23 m (0.75 ft) above the floor of the furnace and since the staged air pipes were located on a diameter outside that of the burner tile injection heights of less than about one foot above the heater floor resulted in impingement of the staged air on the burner tile. Thus, the minimum staging height was approximately 0.3 m (one foot).

The results of staging the combustion air while firing the No. 6 oil/adsorber gas mixture at intermediate load are shown in Figure 9 and 10. While lowering the excess air reduced NO_x by a percentage similar to that obtained firing gas fuel only, the use of staged combustion when firing oil with gas did not produce as large a percentage decrease in NO_x emissions as it did when firing adsorber gas only. The absolute amount of NO_x reduction, however, was about the same for combined fuel firing as it was for gas alone. For example, for the case of staged combustion air combined with lowered excess air firing oil and gas, Figure 9 shows that the NO level dropped from a baseline of 219 ppm, dry corrected to 3 percent O_2, to 166 ppm, dry at 3 percent O_2 for a drop of 53 ppm. For the same conditions firing adsorber gas only at the intermediate load the drop was 46 ppm.

This behavior indicates that fuel nitrogen conversion to NO_x was reponsible for a large fraction of the observed emissions when firing the oil/gas mixture. It appears then that approximately half of the baseline NO_x

emission firing oil with gas is due to fuel nitrogen and half is due to thermal NO_x since NO emissions firing this mixture were about twice those observed firing a nitrogen-free refinery gas. The estimated fuel nitrogen conversion efficiency, based on the ratio of oil to gas in the fuel and the oil fuel nitrogen content (~0.8%), is approximately 19 percent.

Figure 10 shows that NO_x emission decreased slightly as staging height increased firing oil with gas. Very little decrease was observed at heights greater than 1.2 m (4 feet).

During all testing with the staged combustion system operating, careful observation of the flame and furnace draft was made. There did not appear to be any problems with coking of the process tubes and at no time was there any emission of carbon monoxide or unburned hydrocarbons even at 2 percent stack excess oxygen. There were certain instances in which the draft in the convection became slightly positive at the low O_2 condition with maximum staging, however, flashback was never observed. The long term effect of this change in furnace draft in terms of maintenance or operational costs is not yet known.

COMPARISON OF PRESENT RESULTS WITH SUBSCALE RESULTS

Table 3 summarizes the NO_x reductions obtained at the present full scale process heater with the emission reductions observed at the subscale test site. For gaseous fuels the trends are the same for both subscale and full scale tests except that the percentages are somewhat lower in the present data. For tests with oil fuels lowered excess air alone was more effective in reducing NO_x emission than was staged combustion alone - unlike the trend observed in the subscale test where staging the combustion gave a significantly greater NO_x reduction than low excess air. Also, the percentages are much lower for the full scale heater than they were for the subscale heater firing No. 6 oil alone.

The reasons for the lower percentage NO_x reductions firing gas fuel only in the full scale heater are not altogether clear. Furnace bulk gas and wall temperatures were much lower in the full scale heater than they were in the subscale unit (~700°F vs. 1700°F). Residence times, however, were probably longer in the full scale heater. The baseline NO emission with the same burner type in the subscale heater firing natural gas was 131 ppm, dry, corrected to 3 percent O_2 compared with the present 105 ppm, which is reasonable in light of the temperature differences mentioned. There may be a decrease in the effectiveness of combustion modifications in reducing thermal NO_x as temperatures are decreased. The mixing of the combustion air and fuel may have been different enough to cause the changes in NO_x reductions from subscale to full scale. The precise location, angle of injection, and spray angle associated with the staged air system are probably also important parameters in the NO_x reduction process.

Unfortunately, direct comparisons of the oil-firing results are not valid since the full scale unit was firing a considerable amount of gas along with the residual oil. In the subscale tests no gas was fired with the oil. Although the fuel nitrogen in the subscale tests was much lower (~0.3%) than it was in the full scale tests, the apparent fuel nitrogen conversion in the former tests was about twice that of the latter. The fractions of thermal and fuel NO_x are thought to be about the same in either case-about 50-50. Further work is planned to determine whether or not the performance of these combustion modifications can be improved for oil-firing applications.

SECTION 4

COST ANALYSIS

In this paper we will concentrate on the cost analysis of lowered excess air and staged combustion air applied separately and in combination to a process heater with a thermal input capacity of 16.1 MW (55 x 10^6 Btu/h). We will consider only the gaseous fuel application. Costs for oil-fired units will be determined pending the results of further experimentation.

INITIAL CAPITAL COSTS

There is no initial capital cost associated with the lowered excess air (LEA) modification at the levels of O_2 used in the present tests. Such costs would be incurred if operation at stack oxygen contents of less than 2 percent were desired since an automatic oxygen control and analyzer would then be required.

The initial capital costs of a staged air system such as that of Figure 2 are given in Table 4. The installed costs include direct labor and overhead charges at contract labor rates. Required equipment and materials include a high pressure blower, a damper, piping, fittings, valves, stainless steel lances for insertion into the firebox, and temperature and flow measurement probes. Shipping costs are also included.

The annual operating costs for combustion modifications to a full scale heater are given in Table 5. The fuel savings were based on the efficiency increases for the various modifications shown in Table 2 and a market price of natural gas of \$2.50/10^6 Btu. (The latter assumption may not be valid in a case where the refinery uses an off-gas which is not readily marketable and would otherwise be flared. In that case, there would be no cost savings associated with the increased efficiency).

In determining the total annualized costs of combustion modifications several assumptions regarding state and federal taxes, insurance, depreciation method, and financing constraints have been made. These are listed in Table 6 and the total annualized costs for the process heater modifications are given in Table 7.

Note that there are two columns for the staged combustion air (SCA) modification only. The one labelled "4% O_2" applies to the SCA modification at a normal operating condition which results in 4 percent O_2 at the stack. The fuel savings and annualized costs are calculated relative to those of a heater having a 4 percent O_2 condition without staging. For the column labelled "2% O_2" the fuel savings and annualized costs are calculated relative to those of a heater having a normal operating condition of 2 percent O_2 at the stack with no staging. For those refinery heaters which normally operate at ~2% O_2 the column "SCA Only-2% O_2" applies. For those which normally operate at ~4% O_2 the column "SCA Only-4% O_2" applied. The "SCA + LEA" column shows fuel savings and annualized costs relative to a 4 percent O_2 normal operating condition without staging.

One may ask why all process heaters do not operate at 2 percent O_2 rather than 4 percent O_2 since it appears to be cost effective to do so. Refinery gas varies significantly in composition and thus requires a varying amount of combustion air. To avoid the possibility of air deficiency and to minimize the need for continuous operator attention, many process heaters are operated at a higher excess oxygen than would be necessary with a more consistent fuel. With the current need to conserve energy, this practice is being revised by installing oxygen controllers and increasing operator attention.

Table 8 gives the annual NO_x emission reductions and cost effectiveness of each combustion modification. The annual NO_x emission reduction is calculated using the values given in Table 2 for percent NO_x reduction and assuming continual operation at 70 percent capacity for 80 percent of the year. The cost effectiveness is simply the total annualized costs divided by the annual NO_x reduction capability.

Table 8 shows that for a gas-fired heater which normally operates at 4 percent excess oxygen the combination of staged combustion air and lowered excess air is an economically and environmentally attractive modification. Lowered excess air alone is very economical but is only 1/3 to 1/4 as effective in reducing NO_x. For a heater which normally operates at 2 percent O_2 the costs of staged combustion air would not be greatly different from those arising from the use of SCA alone at 4 percent O_2. This cost is, however, much greater than the cost of SCA + LEA.

The question of which modification is most cost effective in a given instance will depend on each individual plant situation and each individual heater. Each plant must determine the following:

1) the credit, if any, it should allow for fuel savings,

2) the normal excess oxygen in the heater, and

3) whether or not a lower excess oxygen can be obtained without additional cost.

SECTION 5

SUMMARY

Combustion modifications proved effective on a natural draft process heater rated at 108 m^3/h (16,250 barrels/day) of crude capacity when firing refinery gas. In addition, heater performance was measured for other fuel mixtures including natural gas and No. 6 oil.

While firing refinery gas a maximum NO_x emission reduction of 51 percent was observed, below a baseline emission concentration of 105 ppm, dry corrected to 3 percent O_2. An increase in efficiency of 2.37 percent was observed for this condition and, in general, efficiency was improved by the application of combustion modifications.

Staged combustion air gave a significant NO_x reduction when firing refinery gas regardless of excess oxygen level. Staging height did not have a major effect on NO_x emissions over the range of 0.3 to 2.4 meters.

The NO_x emissions occurring for the various modification techniques followed the trends observed at the subscale level, however, the percentage reductions were slightly less. In absolute magnitude, the NO_x emission reductions occurring for gas-firing were approximately equal to those occurring when No. 6 oil was included in the fuel. The percentage reductions were less, however, for oil apparently because of the fuel nitrogen conversion.

A cost analysis covering initial capital and annual operating costs, total annualized costs, and cost effectiveness of each of the combustion modifications was made. The results indicate that staged combustion air may be an economically and environmentally desirable modification, however, the cost effectiveness for any single application will ultimately depend upon several factors unique to that situation.

LOCATION 7 - NATURAL DRAFT REFINERY PROCESS HEATER

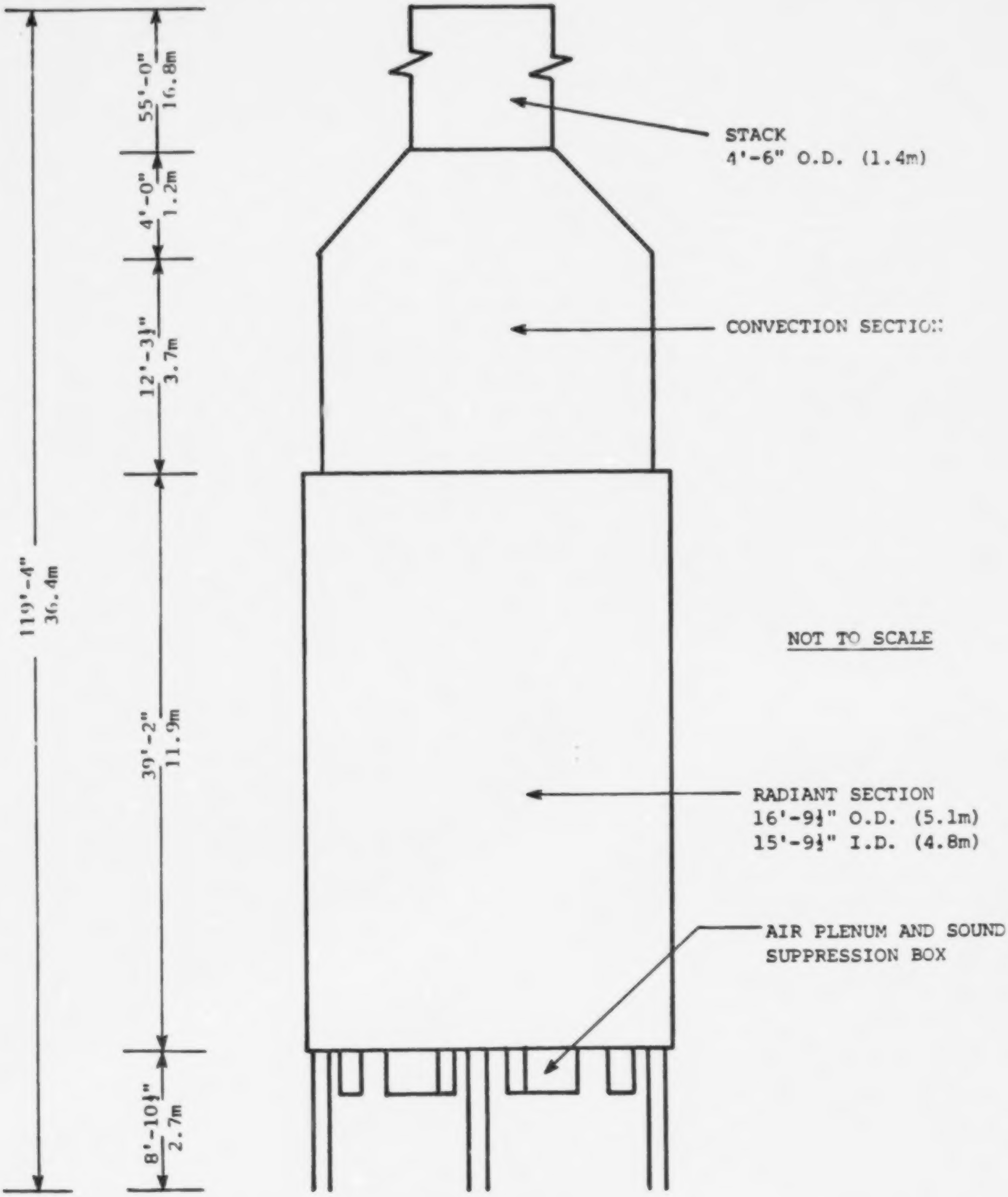
119'-4"
36.4m
55'-0"
16.8m
4'-0"
1.2m
12'-3½"
3.7m
39'-2"
11.9m
8'-10½"
2.7m
STACK
4'-6" O.D. (1.4m)
CONVECTION SECTION
NOT TO SCALE
RADIANT SECTION
16'-9½" O.D. (5.1m)
15'-9½" I.D. (4.8m)
AIR PLENUM AND SOUND
SUPPRESSION BOX

Figure 1. Sketch of the process heater at Location 7.

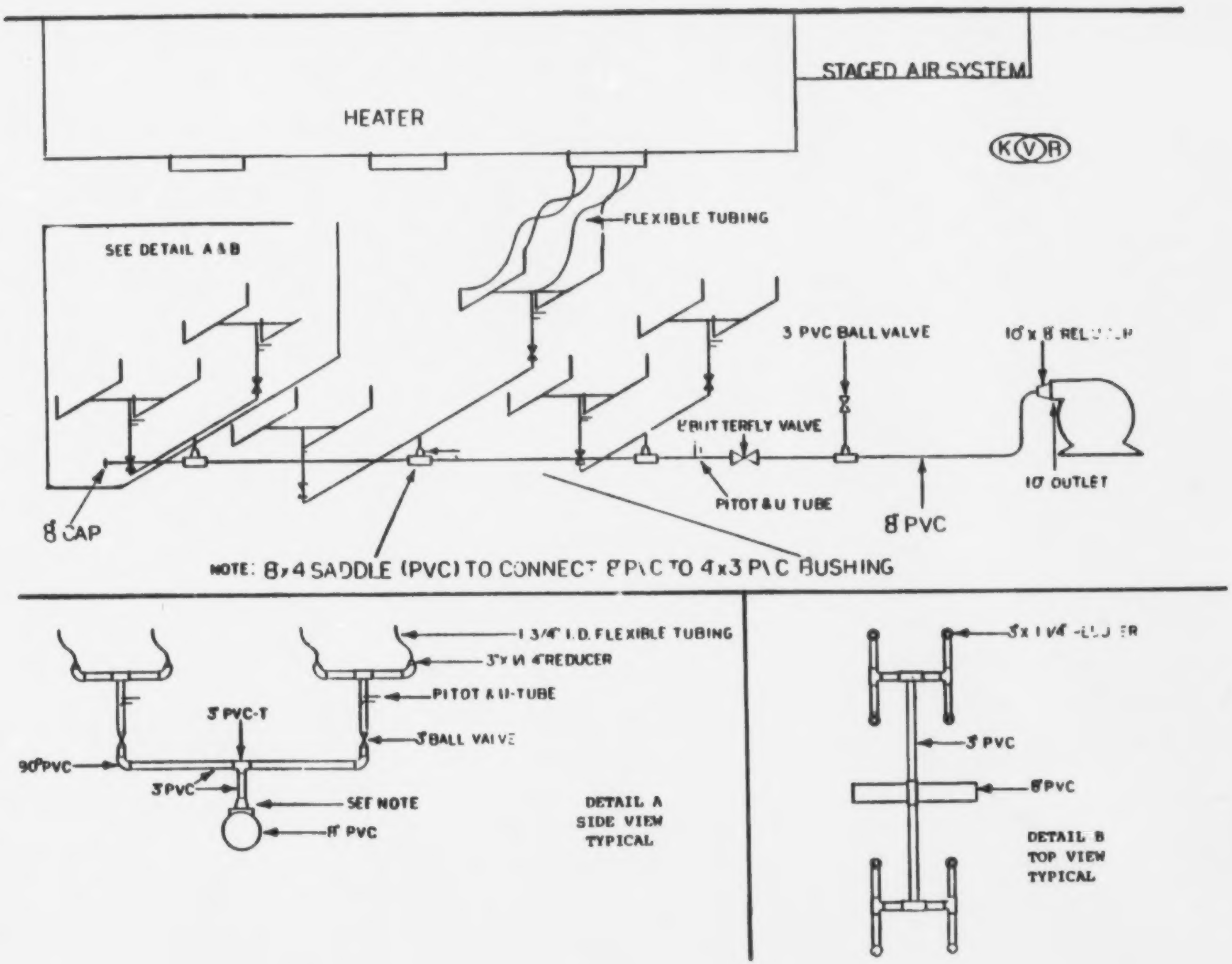
STAGED AIR SYSTEM
HEATER
KVR
FLEXIBLE TUBING
SEE DETAIL A & B
3 PVC BALL VALVE
10 x 8 REL
8 BUTTERFLY VALVE
10 OUTLET
PITOT & U TUBE
8 PVC
8 CAP
NOTE: 8 x 4 SADDLE (PVC) TO CONNECT 8 PVC TO 4 x 3 PVC BUSHING
1 3/4" I.D. FLEXIBLE TUBING
3 x 1 1/4 REDUCER
PITOT & U-TUBE
3 PVC-T
3 BALL VALVE
90 PVC
3 PVC
SEE NOTE
8 PVC
DETAIL A
SIDE VIEW
TYPICAL
3 x 1 1/4 [illegible] ER
3 PVC
8 PVC
DETAIL B
TOP VIEW
TYPICAL

Figure 2. Flow Schematic of Staged Combustion Air System for a Natural Draft Process Heater.

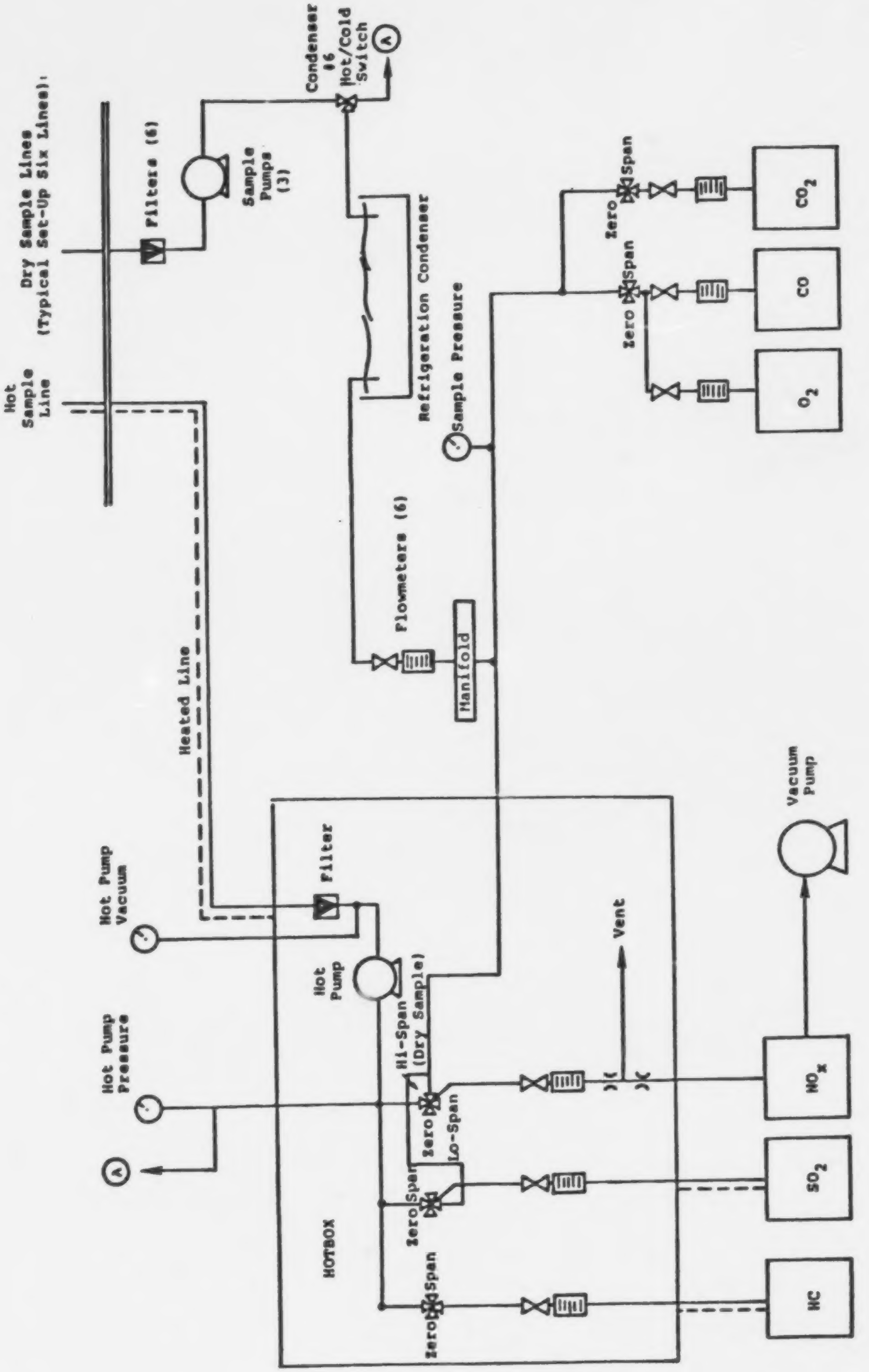
Hot Sample Line
Dry Sample Lines (Typical Set-Up Six Lines)
Filters (6)
Sample Pumps (3)
Condenser #6 Hot/Cold Switch
A
Refrigeration Condenser
Sample Pressure
Flowmeters (6)
Manifold
Heated Line
Hot Pump Vacuum
Filter
Hot Pump
Hi-Span (Dry Sample)
Vent
Vacuum Pump
Hot Pump Pressure
A
Zero
Lo-Span
Zero
Span
HOTBOX
Zero
Span
Zero
Span
Zero
Span
NO_x
SO_2
HC
O_2
CO
CO_2

Figure 3. Flue gas sampling and analyzing system.

NO emissions at three different loads as a function of stack excess oxygen for a natural draft process heater firing a natural gas/refinery gas mixture.

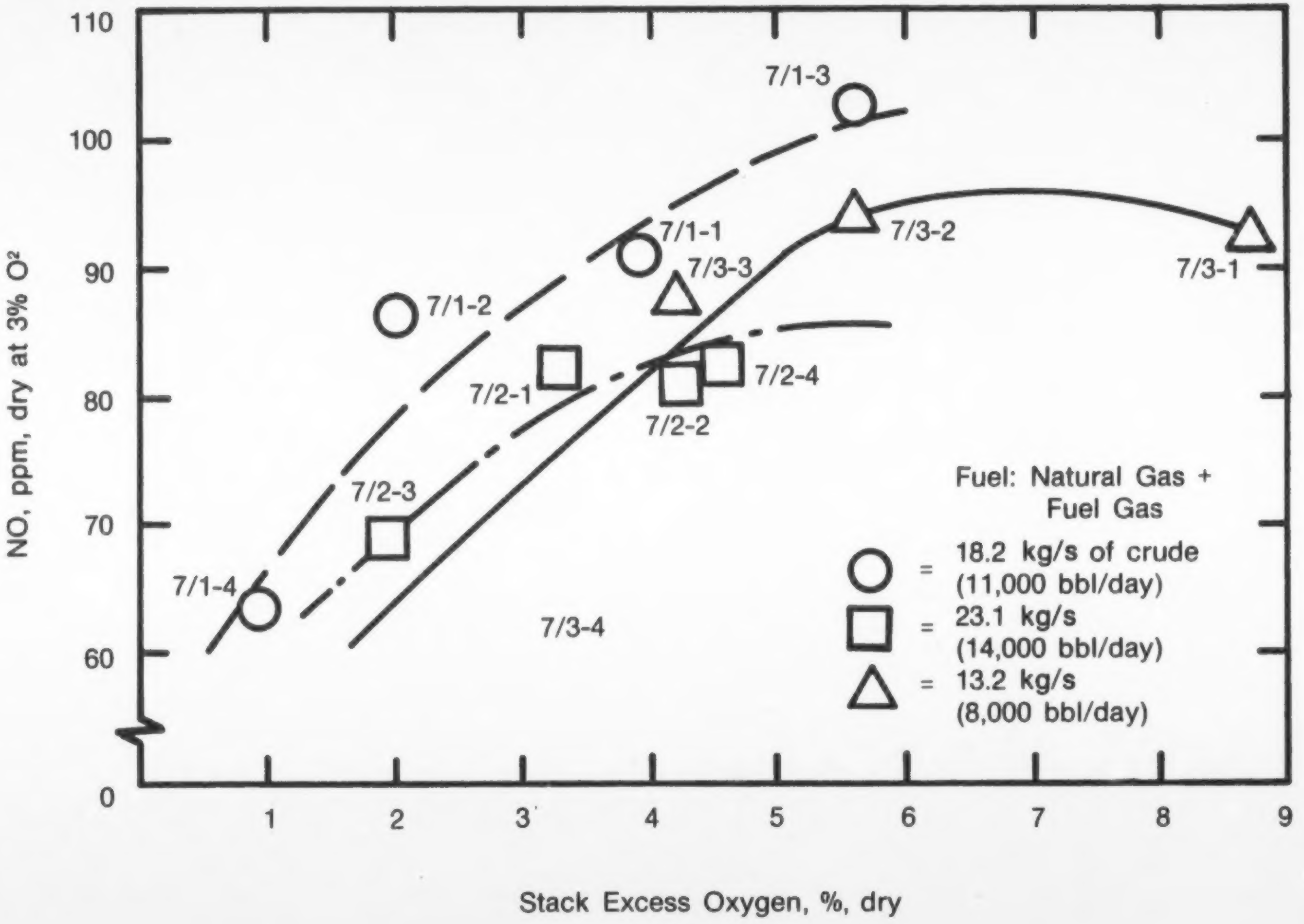

Figure 4.

NO emissions at three different loads as a function of stack excess oxygen for a natural draft process heater.

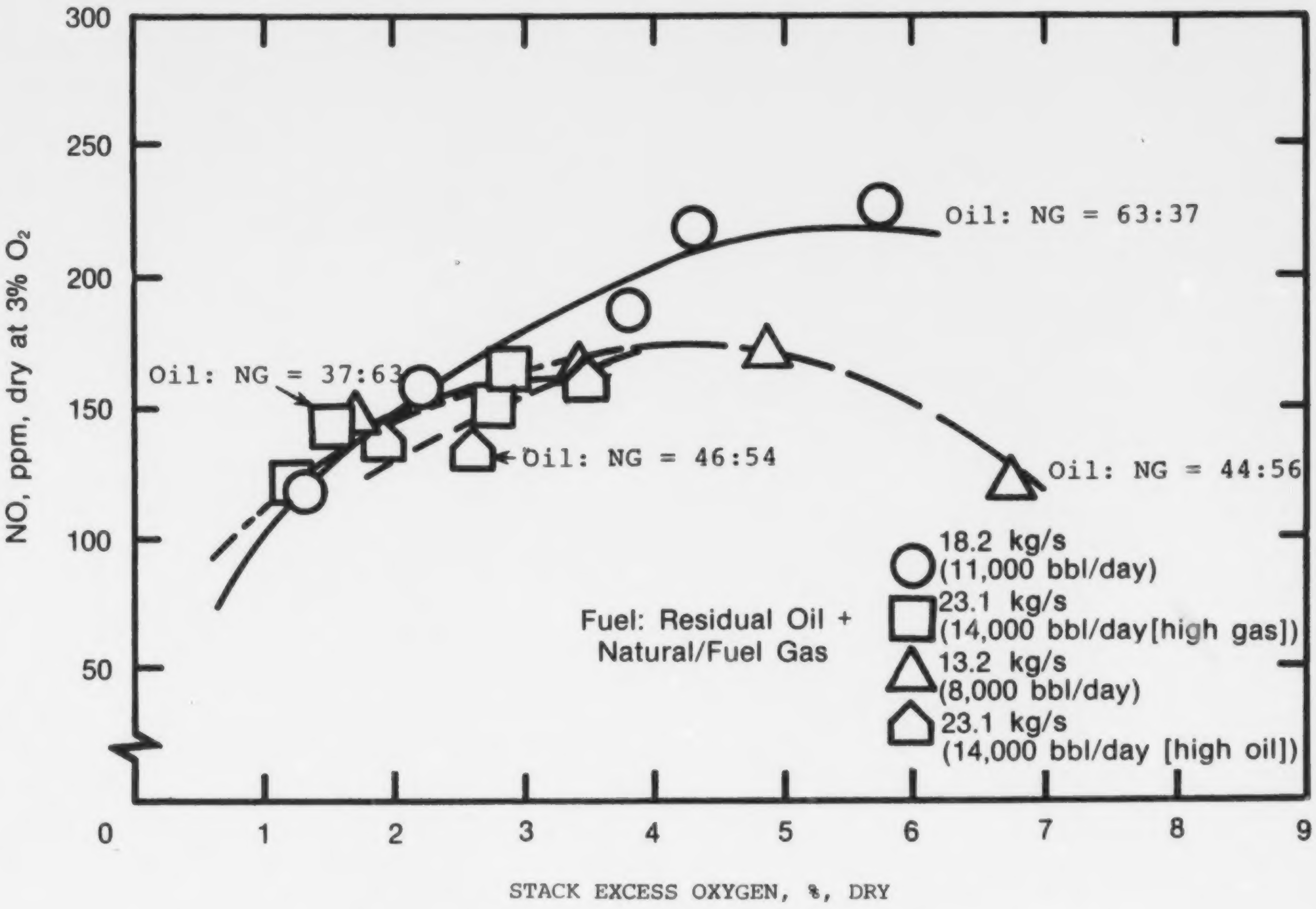

Figure 5.

341

No emissions as a function of burner equivalence ratio at two excess oxygen levels with constant staged air insertion height.

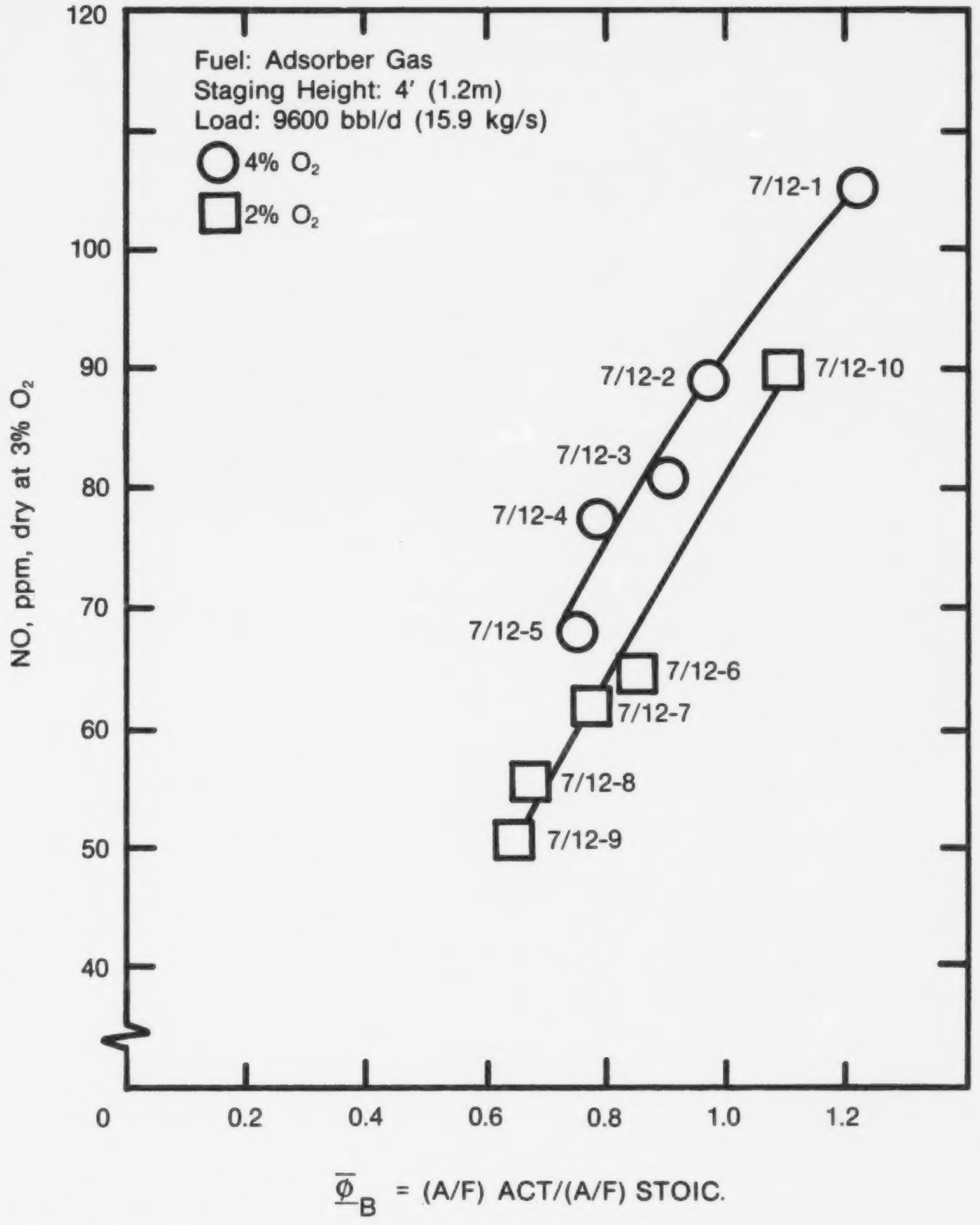

Figure 6.

NO emissions as a function of burner equivalence ratio at two excess oxygen levels with constant staged air insertion height.

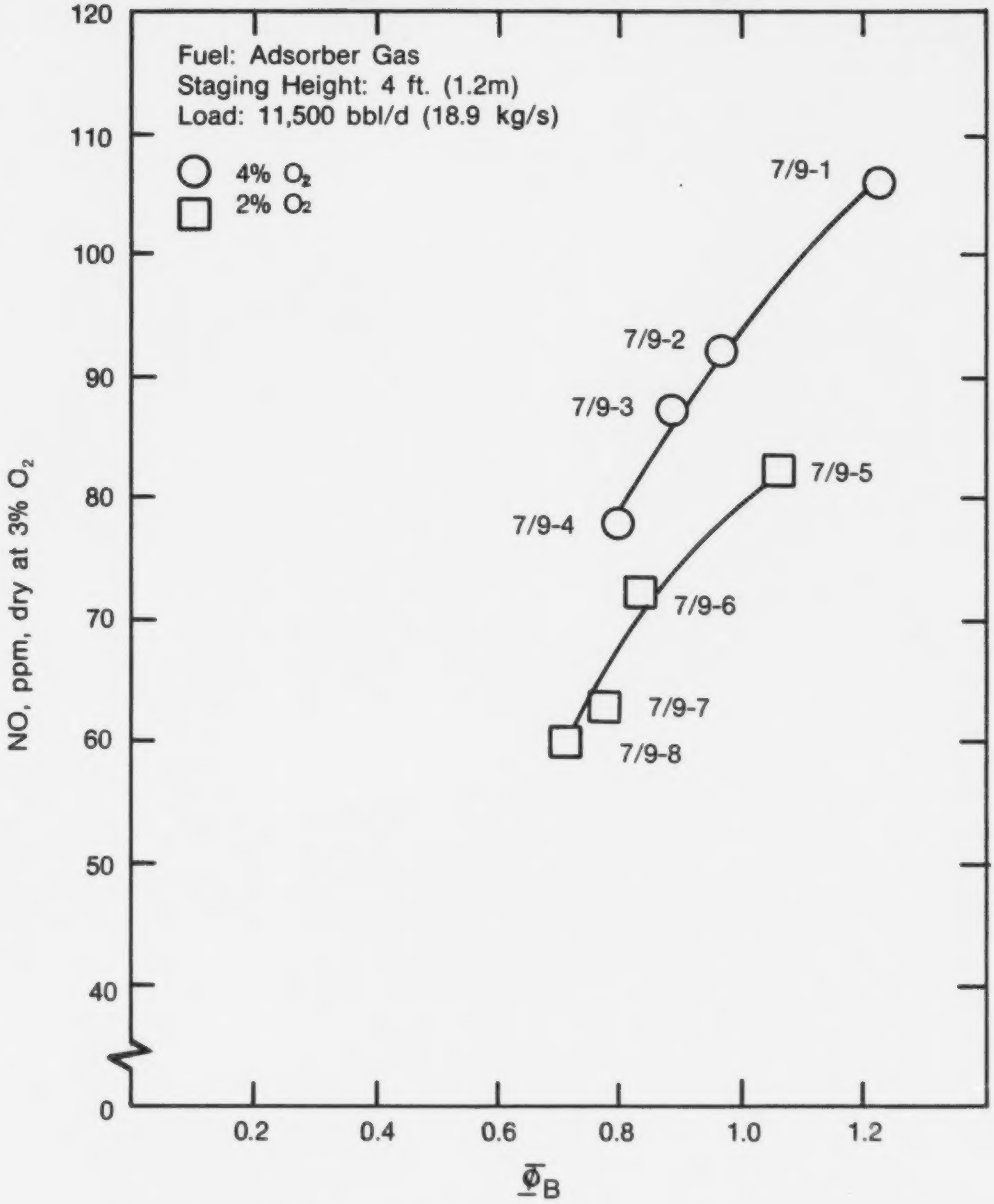

Figure 7.

NO emissions as a function of staging height at constant excess oxygen and $\overline{\phi}_B$.

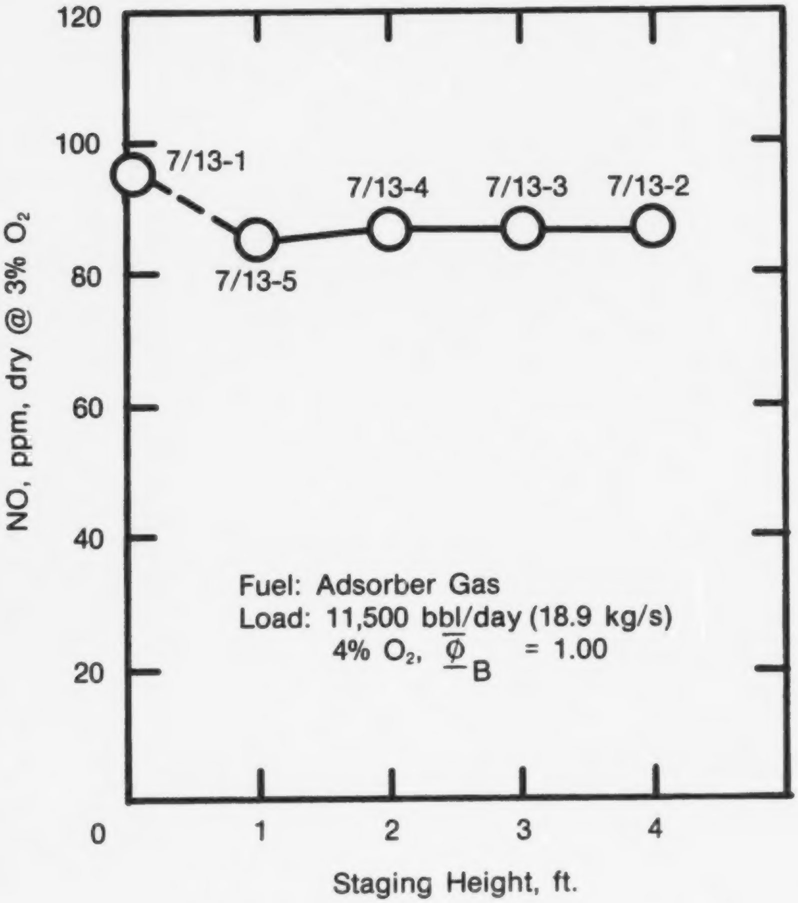

Figure 8.

NOemissions as a function of burner equivalence ratio for a gas-oil fuel mixture.

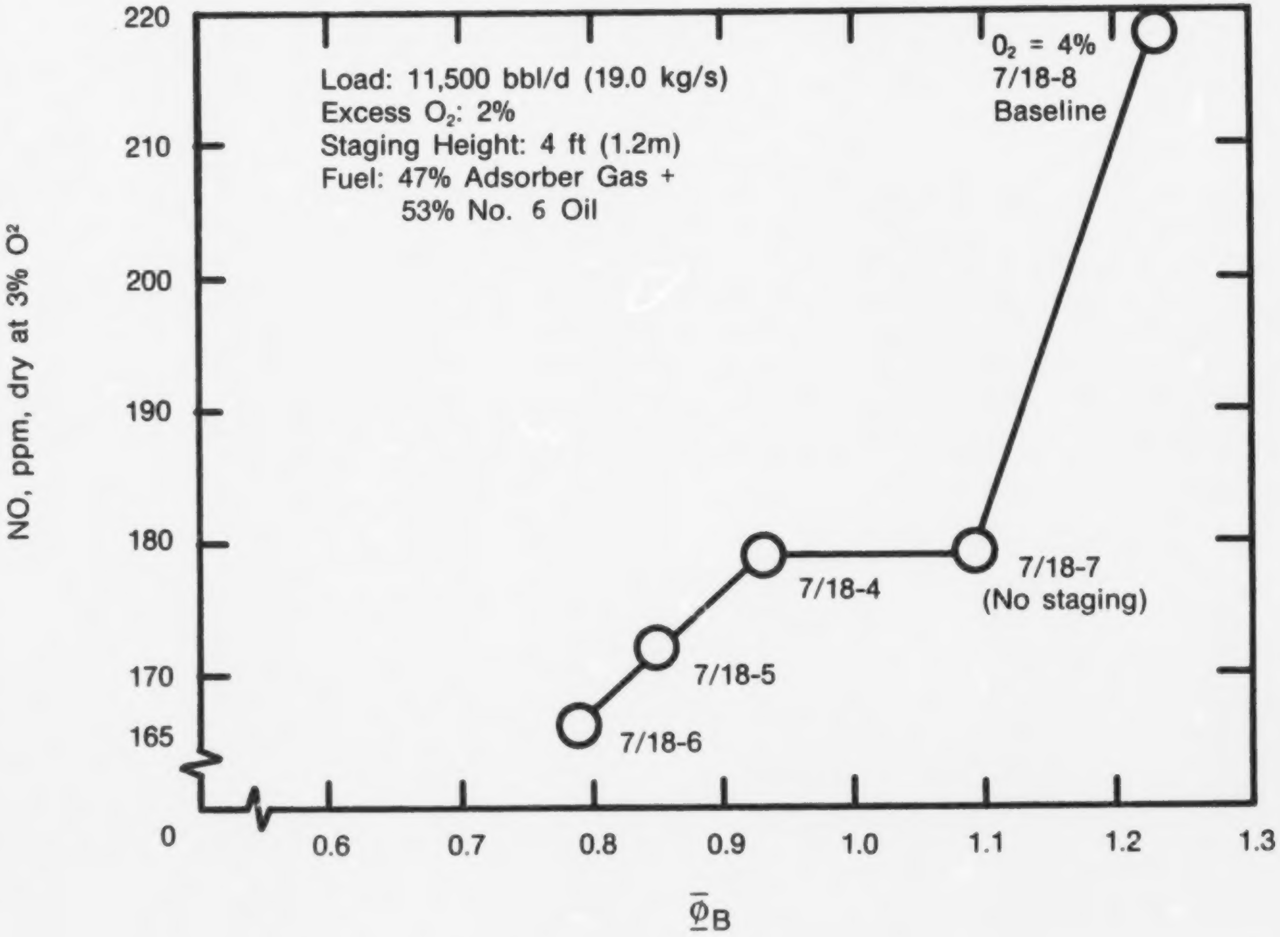

Figure 9.

NOemission as a function of staging height for gas-oil fuel mixture.

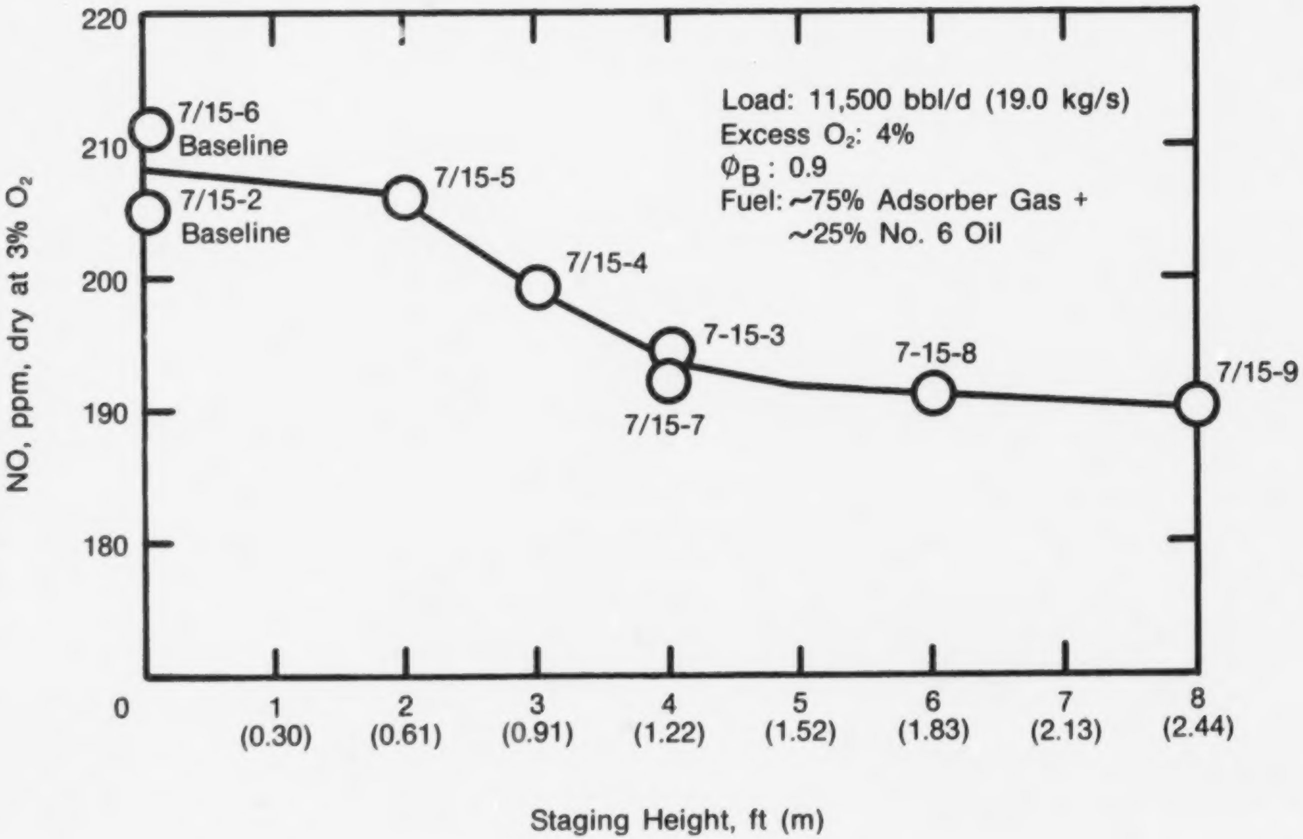

Figure 10.

KINETICS AND MIXING IN INDUSTRIAL AFTERBURNERS

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ABSTRACT

Industrial afterburners can be effective control devices for limiting the emissions of organic species to the atmosphere. For practical and effective operation one must balance the demands of fuel and engineering economics with afterburner size and complexity, operating and maintenance costs, and meeting other specific requirements, such as turndown capabilities. In this paper combustion phenomena in afterburners are considered from the points of view of the turbulent mixing necessary for a compact system and that of the kinetics involved in the reaction process. The mixing aspects are considered first on the basis of the implications of the constructional details of industrially available afterburners, and second from the potential for applying mathematical modeling techniques in the design of more effective afterburners. Examination of the constructional details in terms of the components of generic burner type, approach section, and fume incineration section shows that the mixing phenomenon can be considered from a relatively simple point of view that can be quite amenable to mathematical modeling. The chemical aspects of afterburner systems are analyzed with respect to hydrocarbon oxidation processes. Special attention is devoted to the quasi-global and global kinetics of these oxidation processes. Appropriate equations for calculating chemical performance based on theoretical and laboratory data are examined. Some generalized kinetic predictive procedures are also discussed.

348

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SECTION 1

INTRODUCTION

The afterburner, sometimes referred to as fume incinerator, thermal oxidizer, catalytic oxidizer, was one of the first control devices used by industry. Many industrial processes emit organic fumes of one type of another, and incineration has always been the "obvious" way to eliminate these fumes. How well or how efficiently these afterburners operate was never considered very seriously until the role of organics in the photochemical smog cycle became apparent. At that point it became very obvious that serious steps had to be taken to monitor and control the emissions of these hydrocarbons (organics) (n.b. these two words are often used interchangeably in the context of this paper; they are not synonymous of course, except as their principal oxidation products are carbon dioxide and water vapor).

At the last Stationary Sources Combustion Symposium Barrett and Barnes discussed the nature of afterburner operations. (1) In essence their preliminary environmental assessment showed that in-service afterburners were less efficient than desired, i.e., median efficiencies of 50-75 percent. On the other hand however the lower afterburner efficiency probably had minor impact on national organic nonmethane emissions, but could have a marked impact in local areas.

As a consequence of that work, and as part of this program on afterburner technology it was deemed appropriate to examine the operation of the afterburner in terms of its two key areas--mixing and kinetics. In principle the afterburner is a simple combustion device. Organic vapors, maybe only at concentrations of a few thousand parts per million, coming out of industrial processes, i.e., varnish cookers, paint-bake ovens, degreasing operations, wire-coating, etc., are mixed with air, led into a reaction zone where the temperature is sufficient to oxidize the organic, and the products, CO_2 and water vapor, are emitted to the atmosphere.

This obviously is an over simplistic picture of the afterburner process. Mixing dilute steams of organic vapor with air requires special mixing devices. Bringing the mixture to temperature and carrying out the oxidation can be accomplished several ways, i.e., by passing the mixture (1) through a flame, (2) through a thermal oxidation zone, or (3) through a catalytic reactor. Hence--our interests in this paper in considering the mixing and kinetic processes which influence afterburner design, operation and efficiency.

Conceptually, afterburners can be considered as being divided into 3 sections: an auxiliary fuel combustion section, a fume and combustion product mixing section, and an oxidation (or reaction) section. This afterburner concept is illustrated in Figure 1. Physically, the afterburners sections shown in Figure 1 may be merged and all the processes may occur in one chamber.

In the combustion section, an auxiliary fuel is fired to supply the heat to warm the fume to a temperature that will promote oxidation of the organic vapors. Usually, a portion of the fume stream supplies the oxygen. (Part of the fume stream must be bypassed or the fuel/air mixture will be too lean to sustain combustion.) Both gaseous and liquid fuels are used to fire afterburners. Gaseous fuels have the advantage of permitting firing in multiple-jet (or distributed) burners. Oil combustion has the disadvantage of producing sulfur oxides (from sulfur in the oil) and normally produces higher nitrogen oxides emissions.

The mixing section is designed to provide intimate mixing between the combustion products (from combustion of the auxiliary fuel) and the remaining fume gases. To insure good mixing it is necessary to provide high velocity gas flow to produce turbulence. Gas velocities in afterburners range from 25 to 50 feet per second. Ideally, the temperature profile at the outlet of the mixing section would be flat. In thermal-type afterburners, the following temperatures are often used as guidelines:

Odor control: 900-1350°F

To oxidized hydrocarbons: 900-1200°F

To oxidized carbon monoxide: 1200-1450°F.

The oxidation section provides time for the organic vapors in the bypassed fume to be oxidized. Oxidation sections typically have length-to-diameter ratios of 2 to 3. Depending on the type of pollutant, residence times ranging from 0.2 to 1.0 seconds are required for thermal units. The residence time in most practical afterburner systems is dictated primarily by chemical kinetic considerations.

Catalytic afterburners provide a catalytic surface to promote oxidation for organic vapors. Consequently, catalytic afterburners operate at lower temperatures than the thermal types and require less fuel. The preheat temperature for catalytic devices varies with gas composition and type of contaminant to be oxidized, but is generally in the range from 650 to 1100°F, lower than the 1200 to 1500°F of most thermal afterburners.

A comparison of temperatures required in thermal and catalytic afterburners to convert various compounds to CO_2 and H_2O vapor is given in Table I.

Catalysts in afterburners typically consist of either a metal mesh, ceramic honeycomb, or a ceramic matrix with a surface deposit of finely divided platinum or platinum family metals. In industrial processes, 10 to 100 ft^3 of catalyst bed are used per 1000 scfm of gas flow. In afterburners, however, the requirement is in the range of 1 to 2 ft^3 per 1000 scfm. Catalytic afterburners have the disadvantage that performance efficiency deteriorates as the unit is used, and require periodic replacement of the catalytic material.

SECTION 2

MIXING PHENOMENON IN INDUSTRIAL AFTERBURNERS

The aim in an industrial afterburner is to consume a pollutant down to a safe lower level while balancing the economics of auxiliary fuel requirements, afterburner size and complexity, operating and maintenance costs, and meeting any other specific requirement, such as turndown capabilities. While the kinetics of the specific reactions that are desired establish minimum time-temperature-concentration requirements, the mixing patterns in the afterburners are critical in providing these conditions. Furthermore, the complexities of providing mixing patterns of desired types will control the size of the afterburner, the amount of auxiliary fuel required, and the pressure drop through the afterburner.

The mixing problem in afterburners is considered in this analysis from two points of view. First, the design features of commercially used afterburners are evaluated, from the point of view of their effect on mixing. Second, to provide a basis for evaluating the potential of using mathematical modeling in afterburner design, such use of mathematical modeling is considered. In a future report, the information in the literature on fluid dynamic performance of components of afterburners pertinent to mixing will be reviewed.

DIRECT FLAME AFTERBURNER SYSTEMS

An effective direct flame afterburner provides (a) contact between the contaminants in the air and the burner flame, (b) time for the combustion process to be completed, (c) sufficiently high temperature for the complete oxidation of the combustibles, and (d) flow patterns that ensure adequate mixing while preventing excessive quenching. To accomplish this, the contaminated gases are delivered to the afterburner, where they are mixed with the burner flame or flames in the upstream part of the unit, normally a refractory-lined chamber. They then pass through the remainder of the combustion system, where the combustion process is completed prior to discharge to the atmosphere. Figure 2 is a sketch of a typical fume afterburner using a mixing plate or grid burner. An array of line burners, multijet burner, a nozzle-mix burner, or a premix burner could be used in the same general location. Variations on the recuperator from no recuperator to more extensive ones can also be made. A catalytic afterburner would have the catalyst section inserted at the downstream end of the combustion chamber, and the combustion chamber would not run as hot.

In the following discussion, emphasis is placed on three areas important to the turbulence process; namely, the burner, the approach section to the burner, and the combustion chamber. Since the burner can be an off-the-shelf item, with many other uses, and since it may dictate many features of the approach section and combustion chamber, which are intimately related in construction, the burners are discussed first. The aim at this point is not to consider the details of mixing, but to consider the generic types of components that enter into the mixing portion of an afterburner system.

It will be observed that while a wide variety of each of the components exists, the burners considered as hot gas generators may be reduced to arrays of jets in their influence on mixing. Thus, the fume afterburner systems may be considered to be composed of hot jets and baffle areas, in an environment in which the temperature range is less than in the typical furnace or boiler. This should lead to a simplification of the overall analytical problem for the afterburner designer.

Burners

The purpose of the burner is to provide a hot jet or jets of gas that will raise the temperature of the fume polluted air to the desired level and will also promote mixing of the product gases with the fume polluted air. As much of the fume polluted air as possible is mixed with the fuel gas (or fuel oil) in the burner, to provide "through-the-flame" destruction of the pollutant, and minimize overall system size. On the other hand, to minimize fuel costs, only sufficient heat is desired to provide adequate incineration temperature for the entire polluted air flow. This requirement minimizes the burner(s) size and tends to reduce the amount of primary polluted air. Other conflicting requirements such as minimizing cost by using a small number of burners (maybe one) and minimizing mixing problems by using many small burners enter the problem of burner choice. Finally, an afterburner manufacturer may have the choice of using his own burner design, or a variety of off-the-shelf items. Because the optimum choices are not clear-cut, and vary with type of fume to be incinerated, amount, incinerator location, effectiveness requirements, and fixed and operating costs, there is a wide choice of burner possibilities available in the marketplace.

Six general types of gas burner arrays are distinguished herein: line burners, multijet burners, ring burners, grid or plate burners, distributed source burners, and discrete source burners. Three different types of gas burner mixing systems are also distinguished; namely, premix, delay mix, and nozzle mix. The burner types are discussed below. The sketches are largely adapted from Reference (2) or trade literature.

Line Burners--

Line burners, such as in Figure 3, along with multijet burners and grid burners, are distinguished by being an array of components, and being confined to a rather narrow cross section normal to the flow in the afterburner system. Because these are composed of a multiplicity of elements, their performance may be analyzed on the basis of a single component, with the properly chosen boundary conditions. The components or line elements are made up into lines or grid arrays. Then profile plates are added to block part of the remaining open area, and thus to balance off the air flow between burner elements and the interspaces. As a result, intimate mixing of the fume polluted primary air with the fuel takes place. The fume polluted secondary air is then aspirated into the flame from slots defined by the profile plates along the burner elements. Large recirculation patterns result behind the profile plates; these produce additional mixing.

Multijet Burners--

In the typical multijet burner, such as in Figure 4, small individual raw gas burners aspirate the required amount of fume polluted air to burn as individual flames. An array of these burners is then placed in the combustion duct, with the remaining fume polluted air bypassing the burner array and mixing downstream with the products of combustion. A problem with this system is ensuring adequate mixing downstream, because of the large blockage of the burner array and consequent large distance required for turbulent diffusion and mixing of primary products and secondary polluted air.

Ring Burners--

Ring burners are of the shape implied by the name. Raw gas is impinged on a rod (Figure 5a) or on a ledge (Figure 5b), to stabilize the flames, and increase the rate of mixing. There is no sharp demarcation of primary air and secondary air such as there is in the multijet burner. However, the concept of multiple individual flames is the same.

Grid Burners--

In a grid burner such as shown in Figure 6, a grid perforated with large holes is used to pass the fume contaminated air. On the downstream side of the blockage region, fuel is injected through drilled ports at a low Reynolds number. Some polluted air is recirculated into the blockage region to burn with the fuel. Further fuel combustion may take place immediately downstream, followed by spreading of the flame through the remainder of the fume-contaminated air.

The grid is intended to cover the entire cross section of the combustion duct.

Distributed Source Burners--

The distributed source burner (Figure 7) is quite similar to the multijet burner (Figure 4). However, the burners act independently and the flames are separated by the fume polluted gases moving between the burners. The burners may be either nozzle mix, delayed mix, or premix in type (see below).

Discrete Source Burners--

Discrete source burners, such as shown in Figure 8, may be more economical to build and control. However, the mixing problem is increased as compared to a multiple source system with interspace for the secondary polluted air to come through. The single burners may be placed in an end-wall position, or directed in from a side wall, toward the axis or with some tangential component.

Premix Burners--

A premix burner is defined as a burner in which the gas and air have been previously mixed, or a burner in which the gas and air are mixed before they reach the nozzle.

In a premix burner, the premixed fuel and air are usually supplied to the region from an inspirator or Venturi mixer (Figure 9), an aspirator or suction-type mixer, or a fan mixer. The burner may be a small port or ported manifold type, a large port (or pressure type), a tunnel burner, or a flame-retention type pressure burner. For high firing rates with turbulent flow, the flame will not hold at the end of the duct. Therefore, a variety of flame-holding systems are used. A flame retention type premix burner might be used singly in a large size or as a multiple set in a pattern. Another type of premix burner in which one mixing chamber supplies a multiple set of ports, is similar to the ones used in most residential gas-fired heating units.

Delayed-Mixing Burners--

Delayed mixing burners as those in which the fuel and air leave the burner nozzle unmixed and thereafter mix relatively slowly, largely through diffusion. Figure 10 shows such a burner. This results in a long luminous flame called a diffusion flame, luminous flame, or a long flame. Because of their slow mixing, they are not used as discrete sources in fume afterburners. In smaller sizes as a distributed source, they may be used successfully.

Nozzle-Mix Burners--

A nozzle-mix burner is one in which fuel and air are not mixed until just as they leave the burner port, after which mixing is usually very rapid. Figure 11 shows such a blower. The flame cannot flash back to this type of burner. Nozzle-mix burners combine the advantage of the relatively short flame of the premix burner and the lack of flash-back problems of the diffusion flame. The short flames are obtained by three different methods: (1) multiple high velocity air jets parallel to the fuel jet (the air jets aspirate the fuel in around them and form short flames because of the small jet diameters and potential core lengths), (2) nonparallel impinging or interlacing air and fuel jets (a heavy recirculation zone may be formed, and (3) a burner similar in spirit to (2), but one in which part of the air is mixed rapidly with the fuel, following which the highly turbulent product jet aspirates the remaining air into itself.

Approach Section--

As used in this discussion, the "approach section" and the "combustion chamber" comprise the fume afterburner shell between the heat exchanger components; a generic type of burner would be used to inject the hot products of combustion between the approach section and the combustion chamber. The burner could draw all its fume laden air from the approach section, with the remainder of the fume laden air mixing downstream with the burner products in the combustion chamber, or from a separate supply of either fume laden air or uncontaminated (less economical) air. In any case, the configuration of the approach section has a strong effect on the uniformity of flow the burner(s) and to the secondary air passages, and thus affects both the performance of the burner(s) and the combustion chamber. In other words, the approach section configuration affects the completeness of fume combustion in a given space. Symmetric approaches such as in Figure 8a result in uniformly distributed downstream flows. On the other hand, the turn such as shown in Figure 2 can lead to severe maldistributions. Several of the approach sections that might result in problems are discussed below.

Slotted Duct System--

Figure 12 shows an afterburner approach section with the fume-air mixture being discharged through slots into the products of combustion of a nozzle mix burner. The multiplicity of slots with a reasonable pressure drop should remove the effects of the upstream turns, especially if the duct turns are fitted with properly designed turning vanes. However, considering the cross-sectional view, it is seen that the passage to supply the fume-air mixture to the bottom three slots is rather restrictive. With some designs, the flow through the top slots may be twice that through the bottom slots because of such a restriction. This leads to a maldistribution in the end of the burner tunnel and in the combustion chamber.

We note that Figure 8a shows a variation on slot principle in which orifices supply the fume-air mixture to the burner, and then the remaining fume-air mixture is supplied to the fume combustion chamber by an annulus.

Because of the symmetrical approach section in this case, however, there would be no maldistribution.

Approach With Abrupt Turn--

Figures 2, 5b, 7, and 8b show approach sections with abrupt turns. This may not be a problem with the distributed sources and high pressure drops of Figures 2 and 7. Considering the flow pattern shown in Figure 13b, however, one can see that there could be a severe flow maldistribution in Figure 5b, for example, unless proper precautions were taken by inserting vanes, perforated plates, or other corrective devices, or by providing sufficient combustor chamber volume to compensate for the maldistribution.

High Velocity Approach Section--

Figure 9 shows an extreme case of a high velocity approach section; less extreme cases could also result from too rapid expansion of the supply duct into the burner-combustion chamber system. In the case of Figure 9, a massive recirculation zone would exist around the entrance and extend into the combustion region of the outer burner elements. The ultimate result would be the necessity for a larger combustion chamber section and probably less efficient use of the thermal input.

On the other hand, in some designs, a high velocity product-jet may be desired to aspirate in the fumes, which enter along the length of the jet and intimately mix with the product gases.

Combustion Chamber

The purpose of the combustion chamber in a fume afterburner is to provide the necessary time and temperature to completely consume the pollutants. With perfect mixing of the secondary polluted air with the products of combustion of the fuel and the primary polluted air [well stirred reactor concept in (1)] a simple plug flow system would minimize the rest of the combustion chamber size. Further analysis shows that a minimum total size can be reached with the proper balance of well stirred sections and plug flow sections. Because of various economic and constructional considerations, type of pollutants and variability of supply rates, necessity of turn-down capacity, and other problems, this ideal situation does not exist. Thus there are departures from the ideal solution. In this section, examples of the various types of combustion chambers encountered in practice are considered.

Simple Combustion Chambers--

The simplest combustion system is the rectangular or the cylindrical duct. Figures 2 and 7 show such systems using mixing plate burner and a distributed source burner; Figure 13b shows the use of discrete source burners. With the distributed source, the ideal plug flow situation is closely approximated on a gross scale. With the discrete source, consideration has to be given to the effect of the discrete jet. Figure 14 presents three examples of jet-induced flow patterns. In Figure 14a, the blockage around the entrance results in a recirculation zone with a length of the same order of magnitude as the width. When intense swirl is added, a central recirculation zone is added to the flow pattern (Figure 14b). The third example (Figure 14c) shows that even if there is no blockage, but just a slow velocity uniform stream surrounding a high velocity jet (as from a burner), a recirculation zone can be set up. These recirculation zones may be helpful in moving hot products of combustion upstream where they can serve to start the reaction in the fume polluted air. On the other hand, they take up space that contributes nothing to the needed reaction time.

Combustion Chamber With Baffling--

Combustion chambers such as in Figures 2 and 8b may be equipped with symmetric downstream baffles. These chambers may be circular, or square with baffles on all sides, or rectangular with baffles on two opposite sides. It is obvious that the baffles lead to increased pressure drop. It is not obvious that they necessarily lead to the desired degree of mixing; an annulus of unreacted, partially mixed fume-air mixture could pass through the entire combustion chamber.

Rectangular combustion chambers can also be asymmetric, having one or more bridge walls to mix the products of combustion and the fume-laden air. The gross flow patterns are simple to deduce when zero swirl burners are used. When a high swirl burner is used, the presence of the swirl induces further mixing and a complex flow pattern that may be difficult to deduce.

Side-Fired Combustors--

There are several possible arrangements for side firing a combustor chamber. The gas (or products of combustion) can be fired tangentially into the combustion chamber, resulting in flame impingement on the wall and rapid mixing with the axial flow of fume polluted air through the chamber. There may be single or multiple recirculation annuli, depending on the end conditions of the chamber. The combustion gases may also move in radially and impinge on the opposite wall, and spread in both directions. No net swirl is present. Variations of this design can have multiple entrances.

Compact Combustion Chamber--

The burner flames of Figure 2 may be moved into close proximity with the entrance from the heat exchanger, resulting in a combustion chamber section similar to Figure 13a, in which the flow is turned 180°. This results in a compact recuperator-combustor system. With the distributed combustion, the arrangement does not cause any segregation problems. However, as shown in Figure 13, this 180° turn can result in a reduction in effective residence time by using up volume for the recirculation zone. The same results follow for a configuration with a 90° turn. If a multiple burner or a discrete source burner were used, the abrupt turn can cause an additional problem in obtaining uniform combustion of the fumes.

Regenerative Fume Incinerator--

Figure 15 shows a fume incinerator with a regenerative system for heat recovery rather than a recuperator system (as in Figure 1). Burners fire into the combustion chamber from each end. In each of the three sections shown, fume laden air will flow in one direction (say, downward) through the packed bed, mix with the burner products, burn out the fumes, and then pass into the opposite bed (say, the bottom bed), where heat will be given up to heat the bed. When this bed is sufficiently hot, the entire flow direction is reversed. The fume laden air will be heated as it moves through the hot bed (say, upward through the bottom bed), react with the burner products, and pass through the second bed (top) where the products give up heat. This cycle is periodically repeated. With the direct cross flow of the fume containing gas it is clear that the problem is to ensure good mixing with the combustion products of the burner in the short path available.

SECTION 3

MATHEMATICAL MODELING OF AFTERBURNER MIXING

The purpose of this section is to consider the potential of mathematical modeling techniques in designing more cost-effective furnace afterburners. While many currently available afterburners are based on good design practices stemming from both field experience and research, no examples of the use of mathematical modeling (in the present context) in afterburner design are known. Yet, because of certain characteristics of the afterburners, there appears more potential in using this approach for afterburner design than for many other types of boilers and furnaces.

Considerable progress has been made during the last 20 years in the numerical modeling of turbulent flows, both reacting and nonreacting. (3) The results are generally obtained from the solution of time-averaged conservation equations, in finite difference form. However, if one is not careful, a prediction procedure can rapidly become too expensive for engineering use. Thus, when devising these mathematical models, or choosing a specific model to use, an acceptable balance between economy and accuracy as achieved through physically acceptable simplifications is sought. The scope of this section on mathematical modeling in afterburners is (a) to describe some relevant physical features of turbulence in mixing and reacting flows, (b) to outline the principles involved in the modeling of turbulent combustion, and (c) to suggest a balanced method that could reasonably be employed in afterburner systems studies, stressing particularly the simplifying assumptions involved and their justification. It is not intended to present any detailed or specific programs; these can be developed from the literature references.

This review indicates that, compared to the current level of mathematical modeling problem for combustors, the configuration factors for afterburners may add to the complexity of the problem. On the other hand, kinetic considerations which are only touched on briefly indicate a simple approach to this aspect of mathematical modeling is possible, compared with the usual combustion problem. Furthermore, some physical simplifications in handling the flow problems appear possible.

SOME PHYSICAL FEATURES OF TURBULENCE

The physics of turbulence in any flow system, including that in afterburners, is very complex; yet, the effective use of turbulence is the key to the adequate mixing required in a compact afterburner system. To get the essence of the phenomena across clearly, the present description is quite simplified. For exhaustive treatment, one can refer to Tennekes and Lumley (4) and Hinze (5). Turbulent fluid motion is a time-dependent and inherently three-dimensional condition of flow in which the various quantities show a random variation with time and space coordinates. The momentary value of any property $\tilde{\Phi}$ is conventionally decomposed into an average value Φ and a fluctuation component ϕ so

$$\tilde{\Phi} = \Phi + \phi \quad .$$

Vortex Stretching

A turbulent flow contains a spectrum of vortex (eddy) sizes; the largest are the order of magnitude of a characteristic flow dimension, the smallest are only two or three orders of magnitude larger than the molecular free path length. The large eddies are the "youngest"; their energy is derived primarily from the mean rate of strain in the flow. The vortices are "stretched" by the viscous interaction between them: the turbulence is three-dimensional and the tendency is for vortices to be stretched along their axes by the relative motion of neighboring vortices whose axes are not parallel to that of the one being stretched (Figure 16a). The stretching process is repetitive, continually producing new generations of smaller eddies, whose rotational speeds increase because of the conservation of angular momentum (Figure 16b). Finally, vortices become so small in diameter that their identities are destroyed by molecular smearing and their energy is dissipated into internal energy (heat). An eddy "lifetime" can be imagined. This is typical of all turbulence: most of the energy is associated with large-scale motions, most of the vorticity (or dissipation) is associated with small-scale motions. The transfer of energy from the larger eddies (smaller velocity gradients) to the smaller ones (larger velocity gradients), brought about by vortex stretching, is called the "energy cascade". At high Reynolds numbers, the fine scale motions responsible for dissipation are isotropic.

Correlations, Scales and Spectra

The time average of a fluctuating variable (1) is defined by

$$\phi = \lim_{T \to \infty} \frac{1}{T} \int_{t_o}^{t_o+T} \tilde{\phi}\, dt \quad . \qquad (2)$$

Time averages (mean values) of fluctuations ϕ and of their combinations will be denoted by an overbar; $\overline{\phi}$ is zero by definition.

Consider two fluctuating variables, $A + a$ and $B + b$. If $\overline{ab} \neq 0$, a and b are said to be correlated; if $ab = 0$, the two are uncorrelated. Figure 17 illustrates this concept. (4) a has the same sign as b for most of the time; this makes $\overline{ab} > 0$. The variable c, on the other hand, is uncorrelated with a and b ($\overline{ac} = 0$, $\overline{bc} = 0$) because it has statistically the same chance of having values of the same or the opposite sign as a and b. The correlation coefficient R_{ab}, defined by:

$$R_{ab} \equiv \frac{\overline{ab}}{(\overline{a^2} \cdot \overline{b^2})^{1/2}} \quad , \qquad (3)$$

gives a measure for the degree of correlation between a and b ($\overline{a^2}$ and $\overline{b^2}$ are the variances of a and b, respectively). If $R_{ab} = \pm 1$, the correlation is perfect.

To get an idea of the length scales of the fluctuating motion we consider the correlation between the same fluctuating quantity (say, velocity component, v, is the y-direction) at two different points in space separated by a specific distance (say, r in the x-direction). The (transverse) correlation coefficient is then given by substituting v at x for a and v at x + r for b. Physically, the correlation with separation r is a measure of the strength of eddies whose length in the direction of the vector $\overline{r}$ is greater than the magnitude of r (since eddies smaller than this will not contribute to the correlation). A typical transverse correlation coefficient is sketched in Figure 18.

A length scale of the eddies could be defined as the distance $\overline{r}$ beyond which the correlation is practically zero. However, a more convenient definition is:

$$L \equiv \int_0^\infty R dr \tag{4}$$

actually called the "integral scale". When we speak of the length scale of the energy containing eddies we mean a length of order L. This value of L will be comparable to that of $\overline{r}$ if the R curve does not deviate too much from the rectangular. The difference becomes substantial if there is a certain constant periodicity in the flow pattern, so that the R curve oscillates about the r-axis at high values of r.

The Fourier transform of the space correlation coefficient is called the wave number spectrum. Much basic theoretical work on turbulence is concerned with the behavior of one- and three-dimensional wave number spectra, representing the average amount of energy of the turbulent motion between wave numbers k and k + dk.* A typical isotropic turbulent energy spectrum is plotted in Figure 19. These spectra are useful when dealing mathematically with the transfer of turbulent energy from the low wave numbers (large wavelengths--eddy sizes) to the high wave numbers (small wavelengths--eddy sizes) where it is dissipated.

TURBULENCE AND COMBUSTION

Because they have the greatest specific surface area, and because the stretching process augments the concentration gradients, almost all the molecular mixing occurs across the interface of the smallest vortices (4). Since the smallest eddies are eliminated by diffusion as rapidly as they descend from larger ones, the vortex decay time is characterized by the time scale of large vortices. Thus the decay time is of the order L/U, where L and U are a characteristic dimension and velocity of the flow.

For a turbulent diffusion flame, molecular mixing is a prerequisite to combustion. Since fuel and air are initially contained in separate eddies, this can only occur after a period equal to the eddy lifetime. Now the latter are usually long: for a typical engineering flow, L/U might be 0.5 (m)/10 (m/s) = 50 milliseconds. The time scale for overall fuel/oxidant reaction is the order, at most, of a millisecond. Therefore, turbulence, and not chemical kinetics, is rate controlling. Similar arguments apply for premixed combustion, except that in this case the mixing is between separate eddies of burnt and unburnt gas.

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*The wave number, k, is $2\pi/\lambda$, where λ is the wavelength.

Consider mixing of two species a and b, with concentration fluctuations $c_a = c_b = c$ (where $\tilde{C} = C + c$). c decreases by molecular diffusion. To an observer moving with the fluid (6):

$$\frac{dc}{dt} = -\frac{D}{\lambda^2} c \quad , \tag{5}$$

where D is the diffusion coefficient, and λ the eddy diameter ($\frac{\lambda^2}{D}$ is the time scale of molecular diffusion). λ decreases by stretching (Figure 9). Its decay is assumed proportional to its dimension and inversely proportional to the time scale of the large scale motion (4),

$$\frac{d\lambda}{dt} \sim -\frac{\lambda U}{L} \quad . \tag{6}$$

Combining (5) and (6) and integrating, with $\lambda = L$ and $c = c_o$ for $t = 0$ (birth of eddy), gives:

$$t_{mix} \sim \frac{L}{2U} \ln \left(1 + \frac{2LU}{D} \ln \frac{c_o}{c}\right) \quad . \tag{7}$$

It can be concluded that the turbulence time scale is of primary importance in the mixing process. The influence of molecular diffusion is secondary, although essential.

FUNDAMENTALS OF TURBULENT COMBUSTION MODELING

The Flow

As already mentioned, turbulent flows in afterburners are three-dimensional and time-dependent. Calculation over their entire length and time scales is both impossible (with available computers), and unnecessary from a practical viewpoint. As a consequence, mean predictions are sought by solving time averaged equations. Making substitutions of the type shown in Equation (1) for the variables in the continuity and Navier-Stokes equations and averaging, unknown correlations of the form-$\rho\overline{U_i U_j}$ appear in the derived flow equations because convective terms are nonlinear. They are apparent stresses (for instance, $-\rho\overline{uv}$ represents an extra mean shear stress on the face dxdz of an infinitesimal control volume with sides dx, dy and dz in the coordinate directions). These extra turbulent stresses are called Reynolds stresses; the time-mean Navier-Stokes equations, in which they appear, are called the Reynolds equations. Turbulence models relate these unknown stresses to known or determinable properties. Having more unknown than equations in the customary description of turbulence is called the "closure" problem.

Much of the work on turbulence modeling employs an isotropic turbulent or "eddy" viscosity concept. This assumes that the turbulent stresses act like the viscous stresses; that is, they are proportional to the velocity gradient. In general form:

$$\rho\overline{U_i U_j} = \mu_t \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) - \frac{2}{3} \rho k \, \delta_{ij} \qquad (8)$$

where δ_{ij} is the Kronecker delta ($\delta = 0$ for $i \neq j$, $\delta = 1$ for $i = j$).

The turbulent viscosity μ_t is not a property of the fluid but depends on the dynamic condition of the flow, and its value varies from point to point. If μ_t could be expressed in terms of known or calculable quantities, then the derived flow equations could be solved.

Prandtl proposed in 1925 (for a simple shear flow):

$$\mu_t = \rho \ell_m^2 \left| \frac{\partial U}{\partial y} \right| \quad , \qquad (9)$$

where ℓ_m is a characteristic length scale of the turbulent motion, called mixing length. ℓ_m must be prescribed algebraically; but in boundary-layer flows, a few simple rules usually serve for its prescription.

Other models require the solution of a differential equation to determine the turbulent viscosity. The local variation of μ_t is assumed to be given by the Prandtl-Kolmogorov formula:

$$\mu_t = C_\mu \rho k^{1/2} \ell \quad , \qquad (10)$$

where k is the turbulent kinetic energy and C_μ is a constant. In this model, the length scale ℓ is still prescribed algebraically. On the other hand, k is determined from the solution of a differential equation expressing the processes by which it is transported.

Two-equation models of turbulence require the solution of two transport equations, one for k and another one for a quantity from which ℓ can be derived. These models employ for μ_t the same formula prescribed above. They do not require ℓ be prescribed algebraically, and this is an advantage in modeling flows with recirculation, in which it is rather difficult to determine the length scale profile by measurement.

More advanced models do not introduce the turbulent viscosity concept, but involve the solution of transport equations for the Reynolds stresses. This is probably the optimum level of closure in terms of physical interpretation, and it has the potential to be generally applicable to a wide range of flows. However, Reynolds stress closures are still in a development stage, and are computationally very expensive.

Equation (10) contains the constant C_μ, and other constants appear in the transport equations for k and other variables of the turbulence models. These "constants" are semiempirical quantities, derived by matching experimental and numerical results by computer optimization. They are functions of the specific model employed, and for the same model they depend on the type of flow solved, and sometimes vary with the various investigators. Therefore, when applying one model of turbulence, care should be taken to employ the set of constants which is appropriate to the model and the flow type.

The specification of a length scale ℓ is a dimensional necessity which stems from the derived flow equations and the assumption of Equation (10). This scale can be visualized as being the size of the largest eddies of the flow, and thus having the order of magnitude of an integral scale L [Equation (4)]. This of course does not imply that a single value of ℓ can be assigned at each point for a specified flow condition. The actual value of ℓ will be a function of the specific turbulence model employed. However, it is plausible that length scales predicted with different models will be locally of the same order of magnitude.

Thermal and Chemical Properties

In the afterburner design considerations, the boundary can be fixed to exclude the burner reaction region up to the point where the secondary fume laden air mixes into the products. As a result, the thermal and kinetic considerations can be simplified. Nevertheless, when dealing with a nonisothermal reacting system, the conservation of energy and a conservation equation for each significant chemical species have to be considered. Again using scalar quantities of the form of Equation (1) for the composition terms, conservation equations are produced in which terms similar to the turbulence stress terms appear. A turbulence model is now required to cover these additional terms.

Any detailed chemical model describing the combustion of higher hydrocarbons should take into consideration a large number of species and reaction steps. Each species involved in the modeling of the chemical kinetics necessitates the solution of an additional conservation equation, and hence increases the computer time required. Moreover, uncertainties exist in both the mechanisms and the reaction rates for the various species. For these reasons it is common practice to assume a global, one-step reaction between fuel and oxidant. This simple assumption allows the heat release rate to be well evaluated, but cannot be used to predict pollutant formation and emissions. Improvement is possible by supposing a two-step reaction in which the hydrocarbon reacts to form CO and H_2O followed by the oxidation of CO to CO_2 (7). A three-step mechanism was used by Arbib, et al. (8), for hydrocarbon attack (to CO and H_2), CO oxidation and water formation. All the above-mentioned investigations employed global reaction rate expressions.

Instantaneous global reaction rates are usually expressed as

$$\tilde{R}_j = \tilde{K}\,\tilde{C}_{fu}\,\tilde{C}_{ox} \quad , \tag{11}$$

where $\tilde{K}$ is the rate constant, usually written the Arrhenius form. The time-averaging of $\tilde{R}_j$ represents one of the central difficulties of combustion modeling. Calculations have often been performed by the simple expedient of expressing the time-averaged reaction rate in terms of the individual average values. But, since the concentration and temperature fluctuations can be large, this practice is not, in general, justifiable. In addition to the highly nonlinear dependence of reaction rate on temperature, a situation can occur in which the instantaneous values of fuel or oxidizer concentrations vanish for finite periods of time, leading to a time-average rate of reaction which is less than the one computed using time-averaged values of the concentration (the "unmixedness" problem).

The Computation

Once the differential equations have been set up, they have to be solved numerically. To this end, adequate algorithms exist today. They usually involve writing the conservation equations in a common form, and solving them by the finite difference procedure.

Computational codes to solve these equations are described by Gosman, et al. (9), and Gosman and Pun (10), for two-dimensional recirculating flows; by Patankar and Spalding (11), for boundary-layer type flows; and in the TEACH-3E program developed at the Imperial College (and so far unpublished for three-dimensional recirculating flows. A considerable degree of sophistication is being achieved by using these techniques to predict combustor performance, with a fair amount of success (12).

RECOMMENDATIONS

Because of the great variety of afterburner systems and the wide range of fuel and waste gas combinations in them, it is rather difficult to choose a specific model which would suit all or most of them. However, a number of recommendations can be made in the light of previous experience.

Flow Geometry

Most industrial afterburners have a complicated geometrical form, and the flow in the combustion region presents zones of recirculation. Therefore, in principle, the full three-dimensional conservation equations would need to be solved. Although methods are available for doing that, they would be presently uneconomical for applications of this kind. Moreover, in many combustion chambers the burners generate in their immediate vicinity very nearly axisymmetric flames, which are often relatively insensitive to the details of the flow elsewhere. This would suggest that a two-dimensional procedure for axisymmetric flows with recirculation would be suitable for most afterburner systems. This would lead to elliptic conservation equations in cylindrical-polar coordinates.

Turbulence Model

The most established turbulence model to date is the two-equation model in which equations are solved for the turbulence kinetic energy, k, and its dissipation rate, ε. The turbulent viscosity may then be related to k and ε by dimensional arguments as

$$\mu_t = C_\mu \rho \frac{k^2}{\varepsilon} \tag{12}$$

where C_μ is a constant of the model. The effective exchange coefficient $\Gamma_{\phi,\mathrm{eff}}$ for a variable θ may be expressed as

$$\Gamma_{\phi,\mathrm{eff}} = \frac{\mu_{\mathrm{eff}}}{\sigma_{\phi,\mathrm{eff}}} \quad , \tag{13}$$

where $\sigma_{\phi,\mathrm{eff}}$ is a turbulent Prandtl or Schmidt number.

Most two-equation models of turbulence provide predictions of roughly the same level of accuracy. The reason why the k-ε model has been favored by more workers than any other lies partly in the relative ease with which the exact equation for ε can be derived, and partly in the mainly esthetic fact that ε appears directly as an unknown in the equation for k. In addition, the equation for ε has the advantage to contain fewer terms. The k-ε model also appears to give better results for flows near walls (13).

A usual approximation is to assume $\sigma_{\phi,\mathrm{eff}} = 1$ in Equation (13) for any variable ϕ. This makes the effective diffusive transport coefficients, $\Gamma_{\phi,\mathrm{eff}}$, all equal (= μ_{eff}) at every location for all variables. This approximation is very good, since usually the σ_ϕ's are all of order unity.

Kinetic Model

The chemical aspects of afterburner systems are reviewed in the next section. All that needs to be stated here is that for some applications, in particular those in which the waste gas contains mostly inerts and only the temperature distribution in the combustor is important, a global, one-step reaction between the fuel and the oxidant is sufficient. CO and H_2 intermediates have a significant role in highly loaded combustors, but is is sufficient to ignore them when one seeks only heat release information. The overall reaction is not influenced by trace species (e.g., NO_x) chemistry. When this approach is not possible, it is of course necessary to keep the number of chemical species involved to a minimum, since every one requires the solution of an additional differential equation.

The time averaged reaction rate could be acceptably approximated by using individual term averaged terms in Equation (11), in applications of this kind. This is because, due to the minute fuel concentrations, the chemical kinetics is relatively slow and the fluctuations in concentration are smoothed out by mixing (14). Moreover, use of a term average version of Equation (11) would plausibly be justified whenever global reaction-rate expressions are employed, if these were determined experimentally through average concentration and temperature measurements inside a combustor having a configuration similar to the one being modeled.

372

SECTION 4

KINETIC PROCESSES IN AFTERBURNERS

OXIDATION CHEMISTRY OF AFTERBURNER SYSTEMS*

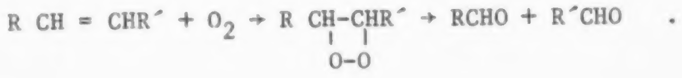
Hydrocarbons in the gas phase react very slowly with oxygen at temperatures below 200°C; however, as the temperature is increased a variety of oxygen-containing compounds begin to form. As the temperature is increased further, CO and H_2O are formed as major products and compounds such as CO_2, H_2O_2, and CH_2O begin to appear. In the range from 300 to 400°C a faint light often appears. This may be followed by one or more blue flames that successively traverse the reaction vessel. At yet higher temperatures, 500°C or above, explosive reactions can occur.

Hydrocarbon combustion at lower temperatures is usually initiated by the reaction

$$RH + O_2 \rightarrow R\cdot + HO_2 \quad .$$

Methane, the simplest of the paraffin hydrocarbons, requires some 40 or more kinetic reaction steps to account for its rate of oxidation. Methane, as essentially all hydrocarbons, is oxidized via an overall two-step set of reactions--first the conversion of methane to CO, and second the oxidation of CO to CO_2.

As the complexity of the hydrocarbon changes, i.e., unsaturated hydrocarbons, aromatic hydrocarbons, the type and number of intermediate organic species increases. Thus aldehydes are formed from unsaturates via



$$R\,CH = CHR' + O_2 \rightarrow R\,\underset{O-O}{CH-CHR'} \rightarrow RCHO + R'CHO \quad .$$

---

*This paper only addresses the homogeneous thermal oxidation processes and does not include catalytic processes. The reader is referred to Reference (15) for a detailed report on Chemical Aspects of Afterburner Systems.

The oxidation of aromatic hydrocarbons in general has not really been investigated extensively. The major steps in the mechanism for benzene oxidation are thought to be

$$C_6H_6 + O_2 \rightarrow C_6H_5 + HO_2$$
$$C_6H_5 + O_2 \rightarrow C_6H_5O_2$$
$$C_6H_5O_2 + C_6H_6 \rightarrow C_6H_5O + C_6H_5 + OH$$
$$C_6H_5O + C_6H_6 \rightarrow C_6H_5OH + C_6H_5$$

The phenol, C_6H_5OH, which forms in high yields because of its great stability is further oxidized to $C_6H_4(OH)_2$, which is in turn oxidized according to the scheme shown in Figure 21. The products on the right in the figure can then be oxidized further. Oxidation of the acetylene generally occurs through a series of chain reactions with formaldehyde and formic acid as intermediates. The high-temperature oxidation of acetylene is also complicated by the tendency of acetylene to polymerize.

QUASI-GLOBAL KINETICS

Kinetically the three controlling parameters for afterburner operation are time-temperature-concentration. Hydrocarbon reactions can be represented globally by the equation

$$C_aH_b + \left(a + \frac{b}{4}\right) O_2 = a\ CO_2 + \frac{b}{2} H_2O$$

where CaH_b is any hydrocarbon. The process of converting C_aH_b to CO_2 and H_2O is kinetically very complex. Kinetic models for hydrogen (17), methane (18) and a number of straight chain hydrocarbons and partially oxygenated organics (19) have been described by a kinetic mechanism consisting of 69 reactions involving 31 species. Edelman and Fortune (20) have taken these complex models and developed a quasi-global finite rate combustion model which reduces the number of steps and species involved, and hence the complexity, in adapting the oxidation models to a wide variety of hydrocarbons.

In general, both the homogeneous gas-phase and catalytic reactions involving the destruction of organics or hydrocarbons in afterburner systems can be represented by the chemical equation

$$\alpha\ F + \beta\ O_2 \rightarrow \text{Products}$$

where F denotes the hydrocarbon fuel and α and β are stoichiometric factors. The chemical reaction rate for the disappearance of the hydrocarbon can be written as

$$\frac{1}{\alpha}\frac{dn_F}{dt} = kn_F^{\alpha}\, n_{O_2}^{\beta} \qquad (14)$$

Since oxygen is in large excess in afterburners this rate expression is readily reduced to a first order rate

$$\frac{1}{\alpha}\frac{dn_F}{dt} = -k'n_F^{\alpha} \quad . \qquad (15)$$

HOMOGENEOUS OXIDATION REACTIONS

Homogeneous Oxidation Rate Data

CH_4--A number of investigators have reported global rate constants for CH_4. Expressions developed by the different investigators are presented in Table II. The equation of Dryer and Glassman is considered to be the best rate expression and is the one recommended here for afterburner applications.

C_2H_6--For ethane oxidation in the presence of excess oxygen the rate expression,

$$\frac{d[C_2H_6]}{dt} = -10^{7.18}\, e^{-32,900/RT}\, ([C_2H_6]_0 - [C_2H_6])^{0.8}$$

was obtained by Glassman, Dryer, and Cohen. (25) The temperature range over which this relationship applies is about 900 to 1050°K.

Higher C_nH_{2n+2} Hydrocarbons--Flame speed and kinetic measurements indicate that oxidation rates for paraffinic hydrocarbons in the series from propane (C_3H_8) beyond decane ($C_{10}H_{22}$) are well within an order of magnitude of those of propane.

The burning rate of propane has been measured in terms of CO_2 formation to be

$$\frac{d[C_3H_8]}{dt} = -2.9 \times 10^{10}\, e^{-15,000/RT}\, f_{O_2}^{0.35}\, f_{CO}\, f_{H_2O}^{0.4} \left(\frac{P}{RT}\right)^{1.75} \text{ moles/cm}^3\text{-sec}$$

where f represents the mole fraction. (26) The temperature range over which the data were obtained was from about 1400 to 1800°K.

Using the detailed chemical kinetic mechanism of Chinitz and Bauer (27) which involved 31 chemical species participating in 69 elementary reaction steps, Edelman and Fortune (20) give the overall rate expression for propane oxidation as

$$\frac{d[C_3H_8]}{dt} = -k[C_3H_8]^{0.5}\ [O_2]$$

where

$$k = 1.8 \times 10^9 \left[\frac{T(°K)}{1111} - 0.5\right] T^{0.5}\ P^{0.2}\ e^{-13,700/RT}$$

with P in atmospheres. The applicable temperature range is estimated to be from 800 to 3000°K, and is based on the conversion to CO and H_2.

Complete combustion to CO_2 and H_2O must take into account the kinetics of the H_2 and CO reactions. A more representative expression for k,

$$k = 5.52 \times 10^8\ P^{-0.815}\ T\ e^{-12,200/T}$$

has been suggested by Glassman (25) and Engelman (28). The above rate expression has also been suggested as being applicable to the overall oxidation of hydrocarbons represented by the generalized chemical equation

$$C_aH_b + \frac{a}{2}O_2 \rightarrow \frac{b}{2}H_2 + aCO$$

with the rate given as

$$\frac{d[C_aH_b]}{dt} = -5.52 \times 10^8\ P^{-0.815}\ T\ e^{-12,200/T}\ [C_aH_b]^{0.5}\ [O_2]\ \text{moles/cm}^3\text{-sec}\ .$$

A general overall mechanism based on the above rate expression is given in Table III.

Nettleton (29) developed a global rate expression for hexadecane. His relationship is based on second order kinetics where

$$k \cong 10^{14}\ e^{-13,200/T}\ \text{cm}^3\text{/mole-sec}\quad .$$

Figure 22 compares Nettleton's rate expression for the removal of hexadecane with Hemsath and Susey's data. (30) The two expressions differ by a factor of 10 in time required for complete removal of hexadecane. For afterburner design purposes however either set of equations allows one to design for effective removal of the hexadecane.

Global rate constants for a number of organic oxidation reactions compiled by Seshadri and Williams (31) are listed in Table IV. In general there is a strong similarity in the rate constants for the different species.

Hemsath and Susey (30) have made oxidation rate-constant measurements in actual thermal-type afterburner systems. Their rate constants, based on first order kinetics, are presented in Table V.

A number of values for activation energies have been reported for various hydrocarbon oxidation reactions. Typically these activation energies range from about 30 to 50 kcal/mole for most organics, and run about 78 kcal/mole for CO. [The reader is referred to Table 17 of Reference (15) for specific values.] Falconer and Van Tiggelen (32) have observed a correlation between activation energies for hydrocarbon oxidation and the weakest C-H bond in the hydrocarbon. These results are summarized in Figure 23. For unsaturated compounds, a reaction at the multiple bond would normally control the activation energy for subsequent branching. In the case of an unsaturated hydrocarbon containing an easily abstracted hydrogen atom, as, for example, propylene, the reaction path with the lower activation energy would be expected to predominate in the chain branching. By extrapolating Figure 23 an activation energy of about 20 kcal/mole might be expected for propylene, based on a carbon-hydrogen bond strength of 77 kcal/mole in the paraffinic portion of the molecule.

Aromatics--Global rate data for the oxidation of toluene based on first-order kinetics are presented in Table VI. The values for benzene given in the table are based on second-order kinetics.

Benzene--

Lee, Jahnes and Macauley (33) have examined the oxidation of several organics, including benzene, in a plug flow laboratory reactor. In Figure 24 we compare their measurements with the expression repeated for benzene in Reference (31). The rate expression of Reference (31) shows fairly good agreement with the measurements of Lee, et al.

Toluene--

Figure 25 presents concentration-time plots for the oxidation of toluene comparing Hemsath and Susey's laboratory data with their derived rate expression and with another expression [Reference (34)]. The plots show a significant difference in the reaction time plots suggesting that the expression in Reference (34) may have too high an Arrhenius factor.

CO--A number of investigators have determined global rate constants for CO oxidation. The important CO oxidation reaction is

$$CO + OH \rightarrow CO_2 + H$$

with the direct oxidation reaction

$$CO + O_2 \rightarrow CO_2 + O$$

being very slow.

Rolke, et al. (2) and Williams, et al. (35) have reviewed the early global rate data for CO oxidation. Selected results and more recent data are summarized in Table VII. A marked variation is observed in the different rate constants. The only actual afterburner rate data for CO are those by Hemsath and Susey. (30) These latter results are recommended for afterburner design applications.

PREDICTIVE METHODS

As one considers the potential number of organics that can be destroyed in fume incineration and, the diversity of chemical structure and reactivity, one wonders whether rate data have to be run on every compound. The answer to this question is yes and no.

In general increasing the number of carbon or oxygen atoms in a molecule or increasing the residence time decreases the temperature requirements. In the other direction increasing the aromaticity or the unsaturation in compounds, results in more stable species and requires higher temperatures for burnout.

Predictive methods for afterburner kinetics have limited usefulness, in part because in more cases than not, mixing may control the overall efficiency of burnout. On the other hand some predictive, correlation techniques are available. Lee, Hansen and Macauley (37) have developed a correlation model for estimating reactivity based on structure and autoignition temperatures of the compound.

Essentially their method calculates destruction temperatures for 99, 99.9, and 99.99 percent destruction from a set of correlation equations, then uses these temperatures to calculate the A and E values in an Arrhenius equation. The correlations work out surprisingly well for the 15 compounds they were able to run in the laboratory.

SECTION 5

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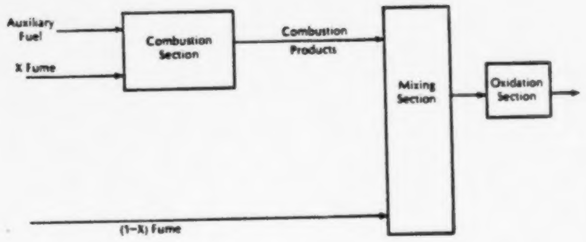

Auxiliary Fuel
X Fume
Combustion Section
Combustion Products
Mixing Section
Oxidation Section
(1−X) Fume

FIGURE 1. SCHEMATIC OF TYPICAL AFTERBURNER

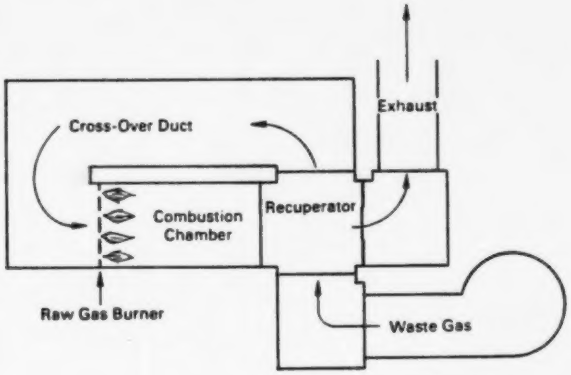

Exhaust
Cross-Over Duct
Combustion Chamber
Recuperator
Raw Gas Burner
Waste Gas

FIGURE 2. FUME AFTERBURNER WITH MIXING-PLATE BURNER AND RECUPERATOR

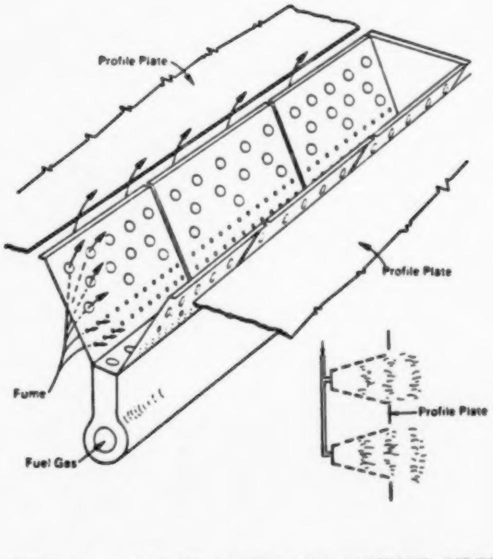

Profile Plate
Profile Plate
Fume
Fuel Gas
Profile Plate

FIGURE 3. MAXON LINE GAS BURNER WITH PROFILE PLATES

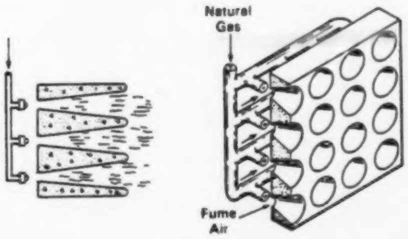
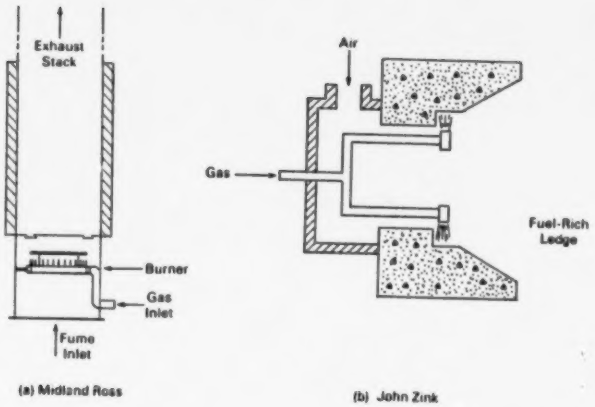

Natural Gas
Fume Air

FIGURE 4. HIRT MULTIJET GAS BURNER


Exhaust Stack
Burner
Gas Inlet
Fume Inlet
Air
Gas
Fuel-Rich Ledge

(a) Midland Ross

(b) John Zink

FIGURE 5. RING BURNERS

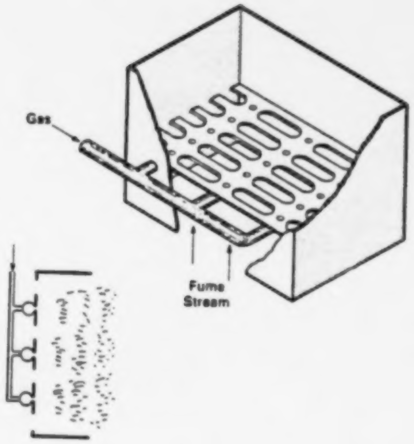

Gas
Fume Stream

FIGURE 6. NORTH AMERICAN FLAME GRID BURNER

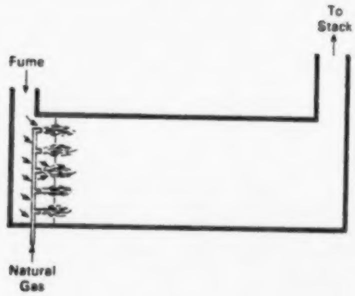

Fume
To Stack
Natural Gas

FIGURE 7. AFTERBURNER WITH DISTRIBUTED BURNER

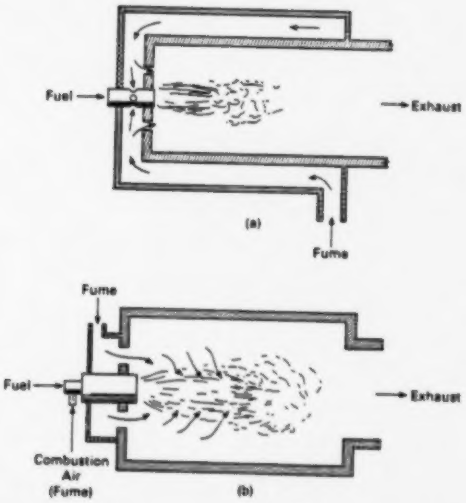

Fuel
Exhaust
(a)
Fume
Fume
Fuel
Exhaust
Combustion Air (Fume)
(b)

FIGURE 8. DISCRETE SOURCE BURNERS

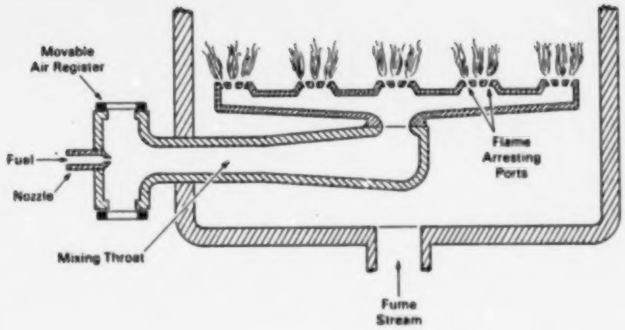

Movable Air Register
Fuel
Nozzle
Mixing Throat
Flame Arresting Ports
Fume Stream

FIGURE 9. PREMIX BURNER

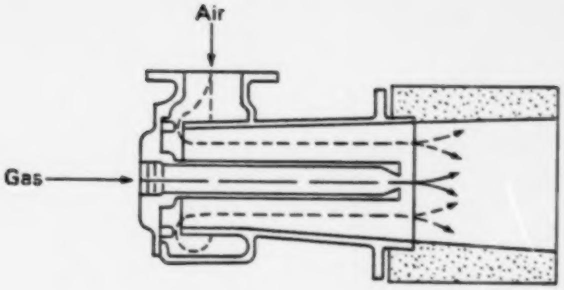


FIGURE 10. DELAYED MIXING BURNERS

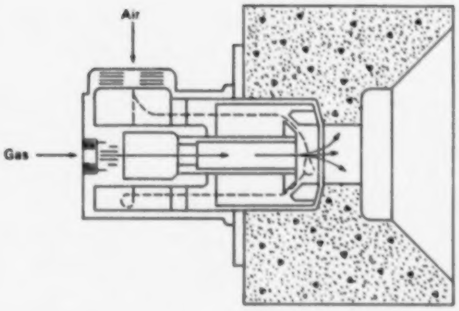


FIGURE 11. NOZZLE-MIXING BURNERS

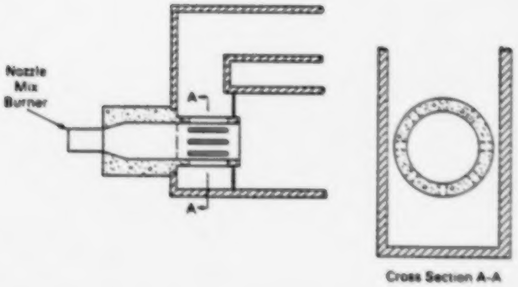
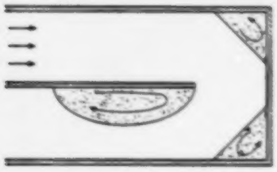
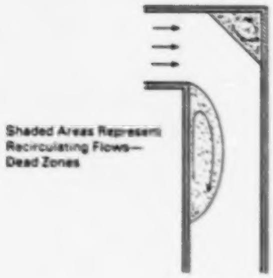

Nozzle Mix Burner
A
A
Cross Section A-A

FIGURE 12. AFTERBURNER APPROACH SECTION WITH SLOTTED DUCT

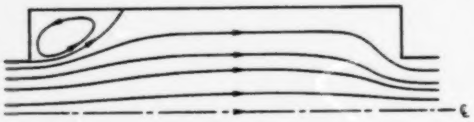


A. U Bend

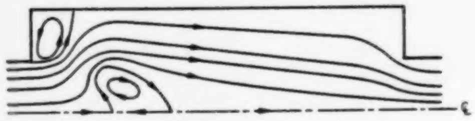

Shaded Areas Represent
Recirculating Flows—
Dead Zones

B. L Bend

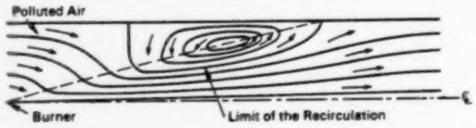
FIGURE 13. RECIRCULATION REGIONS WITH 180° AND 90° TURNS



(a) Low Swirl



(b) High Swirl


Polluted Air
℄
Burner
Limit of the Recirculation

(c) Uniform Low Velocity at Entrance

FIGURE 14. FLOW PATTERNS IN COMBUSTION

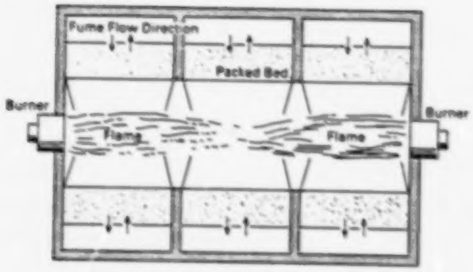
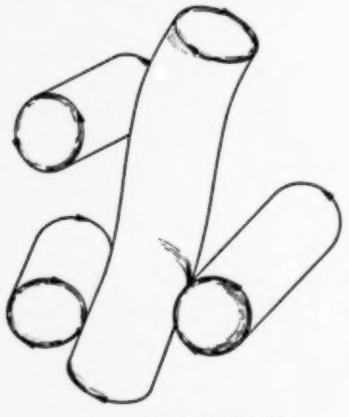
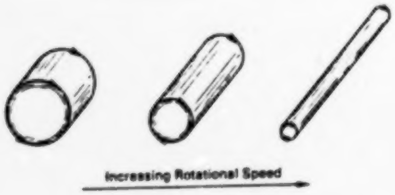

Fume Flow Direction
Packed Bed
Burner
Flame
Flame
Burner

FIGURE 15. PROCTOR-SCHWARTZ SYSTEM WITH REGENERATIVE HEAT RECOVERY

Top View with Ducting Removed



(a) Vortex Stretching Mechanism


Increasing Rotational Speed

(b) Eddy Size Decrease by Stretching

FIGURE 16. VORTEX PHENOMENA

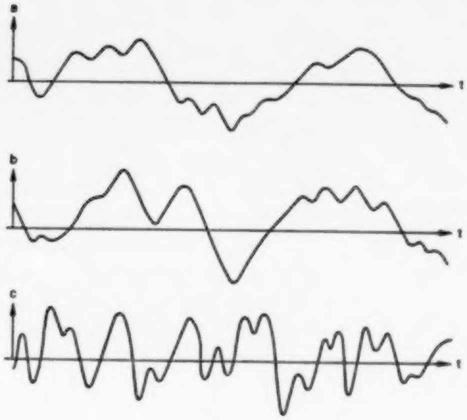


FIGURE 17. CORRELATED AND UNCORRELATED FLUCTUATIONS

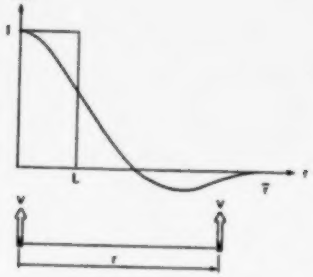


FIGURE 18. TYPICAL TRANSVERSE CORRELATION COEFFICIENT

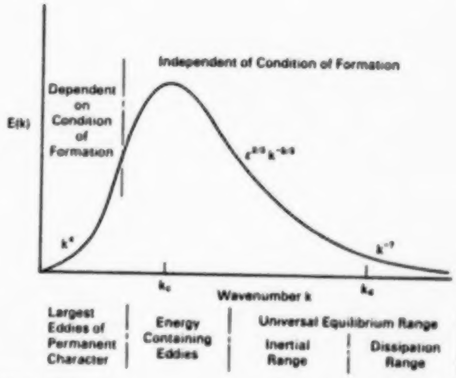


FIGURE 19. TYPICAL ISOTROPIC TURBULENT ENERGY SPECTRUM

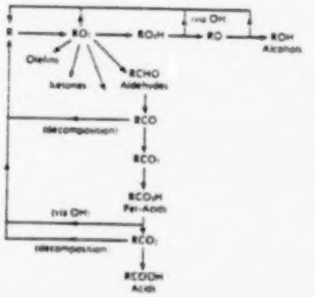

R
$RO_2\cdot$
RO_2H
(via OH)
RO
ROH
Alcohols
Olefins
Ketones
RCHO
Aldehydes
RCO
(decomposition)
$RCO_3\cdot$
RCO_3H
Per-Acids
(via OH)
RCO_2
(decomposition)
RCOOH
Acids

FIGURE 20. SUMMARY OF PRINCIPAL CHEMICAL REACTIONS INVOLVED IN HYDROCARBON OXIDATION

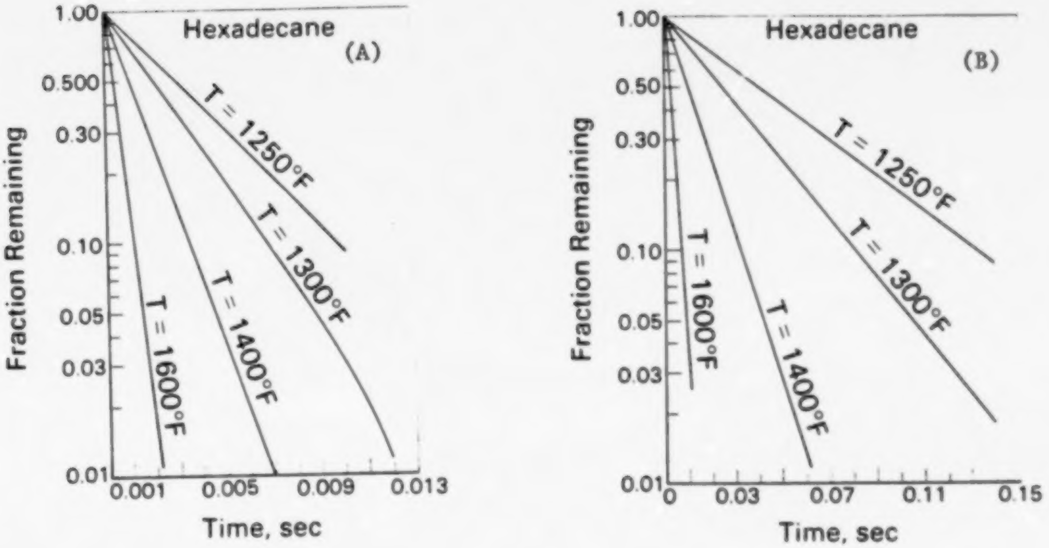


FIGURE 22. HEXADECANE KINETICS
A - Reference 29
B - Reference 30

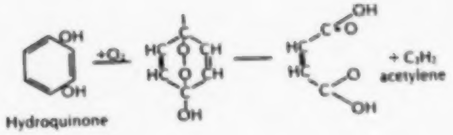

+O₂
Hydroquinone
+ C₂H₂
acetylene

FIGURE 21. REACTION STEPS IN BENZENE OXIDATION THROUGH HYDROQUINONE AS AN INTERMEDIATE

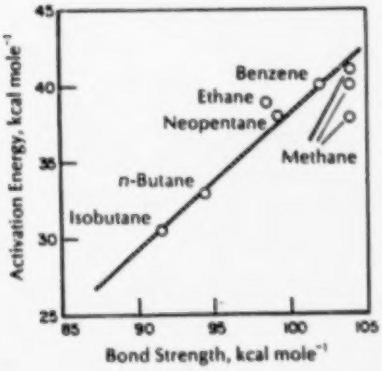


FIGURE 23. DEPENDENCE OF ACTIVATION ENERGY UPON BOND STRENGTH OF WEAKEST C—H BOND(32)

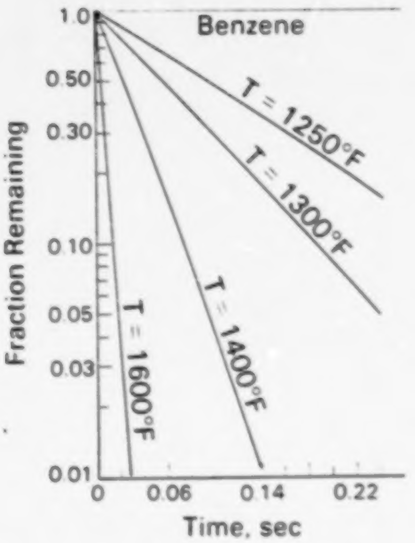
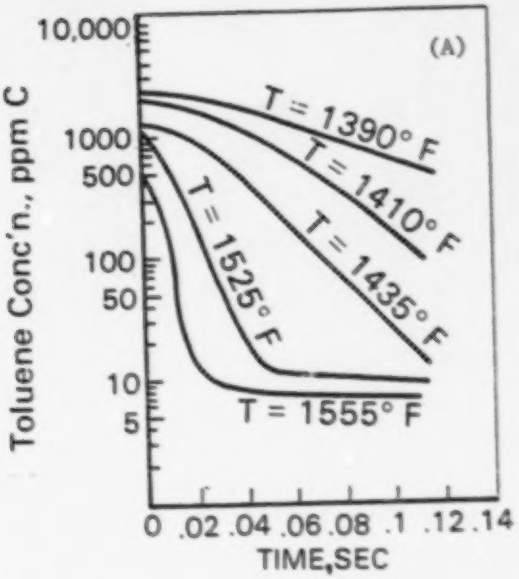


FIGURE 24. BENZENE KINETICS



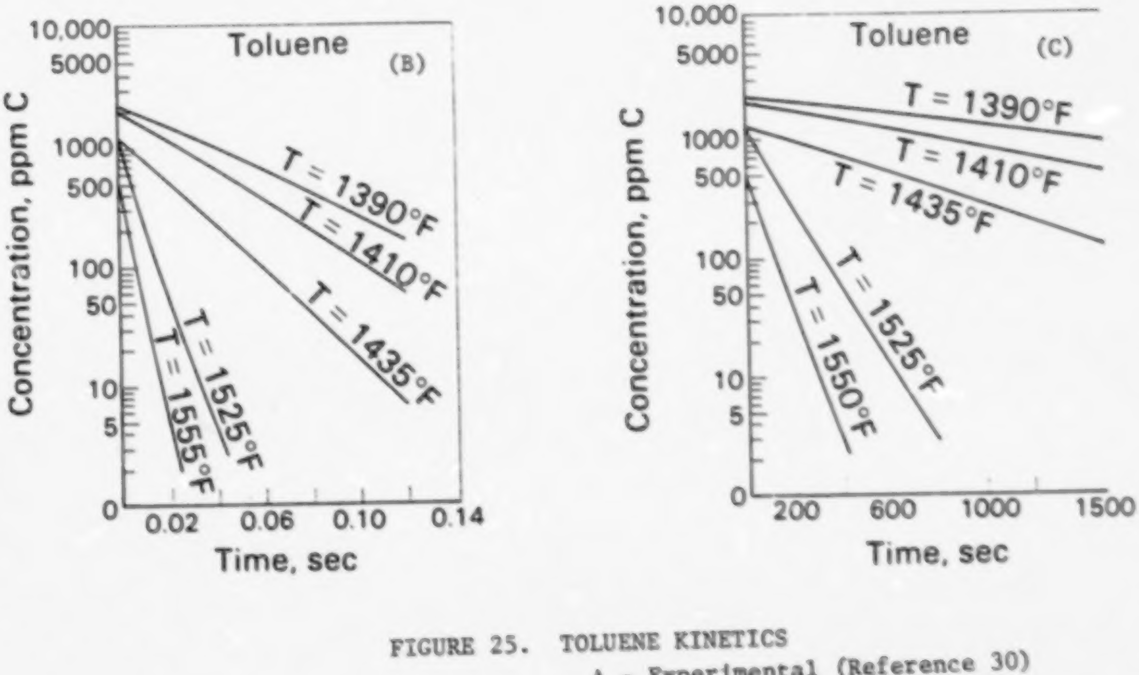


FIGURE 25. TOLUENE KINETICS

A - Experimental (Reference 30)
B - Calculated (Reference 30)
C - Calculated (Reference 34)

TABLE I. COMPARISON OF TEMPERATURES REQUIRED TO OXIDIZE VARIOUS COMPOUNDS TO CO_2 AND $H_2O^{(2)}$

Compound	Ignition Temperature, °F Thermal	Ignition Temperature, °F Catalytic
Benzene	1076	575
Toluene	1026	575
Xylene	925	575
Ethanol	738	575
MIBK	858	660
MED	960	660
Methane	1170	932
Carbon Monoxide	1128	500
Hydrogen	1065	250
Propane	898	500

TABLE II. GLOBAL RATE CONSTANTS FOR CH_4 OXIDATION TO CO

Investigators	Rate Expression	Temperature Range	Reference
Nemeth and Sawyer	$\frac{d[CH_4]}{dt} = -6 \times 10^{10} [CH_4]^{-0.4} [O_2]^{1.4} e^{-57,000/RT}$ mole/cm³-sec	>1200°K	(21)
Kozlov	$\frac{d[CH_4]}{dt} = -7 \times 10^{8} [CH_4]^{-0.5} [O_2]^{1.5} T^{-1} e^{-60,000/RT}$ mole/cm³-sec	1200–1400°K	(22)
Williams et al.	$\frac{d[CH_4]}{dt} = -5.3 \times 10^{15} e^{-57,000/RT} f_{CH_4} f_{O_2}^{0.5} f_{H_2O}^{0.5} \left(\frac{P}{RT}\right)^2$ mole/liter-sec f = mole fraction, and P/RT is in moles/liter	1450–1750°K	(23)
Dryer and Glassman	$\frac{d[CH_4]}{dt} = -10^{13.2} e^{-48,400/RT} [CH_4]^{0.7} [O_2]^{0.8}$ mole/cm³-sec	1100–1400°K	(24)

TABLE III. GENERAL OVERALL MECHANISM FOR COMPLETE OXIDATION OF HYDROCARBONS(20)

$$k = AT^b \exp(-E/RT)^*$$

Reaction	Forward		
	A	b	E/R
$C_aH_b + \frac{a}{2} O_2 \rightarrow \frac{b}{2} H_2 + nCO$	$\frac{5.52 \times 10^8}{P^{0.825}} \cdot C_{C_aH_b}^{1/2} \; C_{O_2}$	1	12.2×10^3
$CO + OH = H + CO_2$	5.6×10^{11}	0	0.543×10^3
$OH + H_2 = H_2O + H$	2.19×10^{13}	0	2.59×10^3
$OH + OH = O + H_2O$	5.75×10^{12}	0	0.393×10^3
$O + H_2 = H + OH$	1.74×10^{13}	0	4.75×10^3
$H + O_2 = O + OH$	2.24×10^{14}	0	8.45×10^3
$M + O + H = OH + M$	1×10^{16}	0	0
$M + O + O = O_2 + M$	9.38×10^{14}	0	0
$M + H + H = H_2 + M$	5×10^{15}	0	0
$M + H + OH = H_2O + M$	1×10^{17}	0	0

*Units: cm^3/mole-sec for bimolecular reactions; cm^6/mole-sec for termolecular reactions.

TABLE IV. RATE CONSTANTS FOR OXIDATION OF MISCELLANEOUS ORGANIC COMPOUNDS(31)

Hydrocarbon Vapor	Chemical Formula	Activation Energy, kcal/mole	Preexponential Factor, cm^3/mole-sec
Isopropyl ether	$[(CH_3)_2CH]_2O$	50	1.2×10^{17}
Butyl-vinyl ether	$CH_3(CH_2)_3OCH{:}CH_2$	31	5.0×10^{14}
Methyl methacrylate	$C_5H_8O_2$	37	2.4×10^{15}
Polymethyl methacrylate	$(C_5H_8O_2)_n$	42	7.6×10^{15}
Methanol	CH_3OH	40	4.6×10^{15}
Heptane	C_7H_{16}	38	2.2×10^{15}
Decane	$C_{10}H_{22}$	37	1.6×10^{15}
Hexadecane	$C_{16}H_{34}$	35	8.2×10^{14}
Iso-octane	C_8H_{18}	35	4.5×10^{14}
Kerosene	$C_{10}H_{20}$ (approx.)	35	5.4×10^{14}

TABLE V. RATE CONSTANTS MEASURED IN THERMAL AFTERBURNER SYSTEM(30)

Compound	Preexponential Constant, k, sec^{-1}	Activation Energy, E_A, kcal/mole
Hexane	4.5×10^{12}	52.5
Cyclohexane	5.13×10^{12}	47.6
Natural gas	1.65×10^{12}	49.3

TABLE VI. GLOBAL RATE DATA FOR THE OXIDATION OF AROMATICS

Compound	Preexponential Term, A	Activation Energy, E_A, kcal/mole	Reference
Benzene	6.0×10^{14} cm^3/mole-sec	36	(31)
Toluene	6.56×10^{13} sec^{-1}	58.5	(30)

TABLE VII. GLOBAL RATE CONSTANTS FOR CO OXIDATION

Investigators	Rate Expression, mole/cm^3-sec	Temperature Range	References
Williams, Hottel, and Morgan	$\frac{d\,[CO]}{dt} = -1.8 \times 10^7\ e^{-25,000/RT}\ f_{CO}\, f_{O_2}^{0.5}\, f_{H_2O}^{0.5}\ (P/RT)^2$	1450–1750°K	(23)
Howard, Williams, and Fine	$\frac{d\,[CO]}{dt} = -1.3 \times 10^{14}\ [CO]\ [O_2]^{1/2}\ [H_2O]^{1/2}\ e^{-30,000/RT}$	840–2360°K	(36)
Dryer and Glassman	$\frac{d\,[CO]}{dt} = -3.9 \times 10^{14}\ e^{-40,000/RT}\ [CO]^{1.0}\ [H_2O]^{0.5}\ [O_2]^{0.25}$	1030–1230°K	(24)
Hottel, Williams, Nerheim and Schneider	$\frac{d\,[CO]}{dt} = -1.2 \times 10^{11}\ e^{-16,000/RT}\ f_{O_2}^{0.3}\, f_{CO}\, f_{H_2O}^{0.5}\ (P/RT)^{1.8}$	1250–1550°K	(26)
Hemsath and Susey	$\frac{d\,f_{CO}}{dt} = -10^{23}\, e^{-100,000/RT}\ f_{CO}\, f_{O_2}^{0.5}\ sec^{-1}$	<1400°F (1033°K)	(30)
	$\frac{d\,f_{CO}}{dt} = -2.5 \times 10^{11}\ e^{-40,000/RT}\ f_{CO}\, f_{O_2}^{0.5}\ sec^{-1}$	>1400°F (1033°K)	(30)

All concentrations [ ] in mole/cm^3. f is the mole fraction.

SUBSCALE TESTS OF COMBUSTION MODIFICATION FOR STEEL FURNACES

(Including Addendum)

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KVB, Inc.
18006 Skypark Boulevard
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ABSTRACT

This is a report of a research program to develop combustion modification technology as means of emissions reduction and thermal efficiency improvement on industrial process equipment. The work is an extension of EPA Contract 68-02-2645, which concentrated on operational adjustments. Presented are results of subscale tests for steel furnaces.

Subscale tests with a standard steel furnace burner firing natural gas and No. 2 oil were conducted to determine the effects on NO_x emission and furnace efficiency of water injection into the flame zone, steam injection into the flame zone, flue gas recirculation, and lowered excess air. With natural gas fuel the largest NO_x emission reduction was obtained using flue gas recirculation (88% reduction). With No. 2 fuel oil the largest reduction occurred using steam injection (89%).

The costs of water injection, steam injection, and flue gas recirculation were evaluated. Steam injection was found to be the most cost effective combustion modification technique for three heater sizes firing either natural gas or No. 2 oil.

SECTION 1

INTRODUCTION

At the Third EPA Stationary Source Combustion Symposium, KVB reported on subscale process heater combustion modification tests. The report summarized the effects on NO_x emissions of several types of modifications, including staged combustion air, flue gas recirculation, lowered excess air, altered injection geometry, and low NO_x burner installation. The work showed that staged combustion air appears to be the most cost effective combustion modification for process heaters. Both staged air and flue gas recirculation produced NO_x emission reductions in excess of 60% below baseline emission levels.

As a continuation of this subscale test work, which is part of a program to develop advanced combustion modification techniques for industrial process equipment, KVB evaluated several of the same combustion modifications on a subscale steel furnace. This paper presents the subscale steel furnace test findings. It is emphasized that these results have not been demonstrated at the full-scale level and, therefore, the modifications cannot now be considered as proven concepts.

OBJECTIVE AND SCOPE

The objective of the program of which these steel furnace tests are only one part is to develop advanced combustion modification concepts requiring minor hardware modifications that could be used by operators and/or manufacturers of selected industrial process equipment to control emissions. The development is aimed at equipment on which the modifications will be most widely applicable and of the most significance in mitigating the impact of stationary source emissions on the environment. The program involves investigation not only of emissions but also multimedia impacts and control cost effectiveness.

The program includes both subscale and full-scale testing. Subscale testing is a necessary part of development of new hardware to ensure acceptable performance, which is a vital aspect of emissions control. Full-scale testing is also necessary on more than one process design configuration (e.g., forced draft and natural draft) before equipment manufacturers and the process industry can employ a given emission control technology.

At the conclusion of the study, a final engineering report will be prepared summarizing the accomplishments of the subscale and full-scale demonstration tests. A series of guideline manuals will be prepared to acquaint equipment manufacturers with the most promising emission control methods that have been demonstrated and to offer technical guidance that can be directly applied in their process equipment design.

MODIFICATIONS EVALUATED

KVB evaluated the following modifications to the subscale steel furnace located at the technical center of a major steel furnace burner manufacturer:

1. Lowered excess air.
2. Steam injection when firing No. 2 oil fuel.
3. Water injection when firing natural gas fuel.
4. Flue gas recirculation.

The details of the experimental arrangement and the results obtained are given in the following sections of this paper.

The cost effectiveness study indicates that steam or water injection offers the best NO_x reduction capability for the least cost. However, flue gas recirculation gives the largest NO_x reduction when firing natural gas. Excess air variations did not affect NO_x emissions significantly except at a high excess oxygen level or a very low excess oxygen level, neither of which is a practical operating condition.

399

SECTION 2

EMISSIONS SAMPLING AND TEST APPARATUS

EMISSIONS SAMPLING

The research steel furnace emission measurements were made with instrumentation, carried in a mobile laboratory, which was described in detail in the EPA Interim Report entitled "Application of Combustion Modification to Industrial Process Equipment," Contract No. 68-02-2645.

Gaseous species measurements were made with analyzers located in the trailer. Particulate emission and size measurements were not made during subscale tests to allow a larger range of test variables for effects on gaseous emissions. These measurements will be made on full-scale units. The emission measurement instrumentation used is listed in Table I.

GAS SAMPLING AND CONDITIONING SYSTEM

The flue gas sampling system uses positive displacement diaphragm pumps to continuously draw flue gas from the stack into the laboratory. The probes are connected to the sample pumps with 0.95 cm (3/8 in.) or 0.64 cm (1/4 in.) nylon line. The positive displacement diaphragm sample pumps provide unheated sample gas to the refrigerated condenser (to reduce the dew point to 35°F), to a rotameter with flow control valve, and to the O_2, NO, CO, and CO_2 instrumentation. Flow to the individual analyzers is measured and controlled with rotameters and flow control valves. Excess sample is vented to the atmosphere.

To obtain a representative sample for the analysis of NO_2, SO_2 and hydrocarbons, the sample must be kept above its dew point since heavy hydrocarbons may be condensible, and SO_2 and NO_2 are quite soluble in water. For this reason, a separate electrically-heated sample line is used to bring the sample into the laboratory for analysis. The sample line is 0.64 cm (1/4 in.) Teflon, electrically traced and thermally insulated to maintain a sample temperature of up to 400°F. Metal bellows pumps provide sample to the hydrocarbon, SO_2, and NO_x continuous analyzers.

TEST APPARATUS

The testing discussed in this report was done in a small research steel furnace with a maximum firing rate of 0.6 MW (2×10^6 Btu/hr) located at the test facility of a major manufacturer of steel furnace burners. Both natural gas fuel and No. 2 oil were fired in a standard burner provided by the manufacturer. A schematic of the experimental apparatus is presented in Figure 1.

The test apparatus consisted of a burner firing into a test furnace, with provisions for flue gas, steam, and water to be introduced into the burner flame. The test furnace served as a combustion chamber with a residence time of about two seconds when firing at 0.6 MW. The furnace could operate at 1978K (3100°F) and was outfitted with numerous access ports for visual observation and temperature measurement. The furnace temperature was maintained at 1533K (2300°F) throughout the test by exposing more or less of the water-cooled probes to the furnace interior. This was done to simulate conditions in an actual furnace.

The 0.6 MW (2×10^6 Btu/hr) burner was used to simulate the commonly used 2.4 MW (8×10^6 Btu/hr) version. The burner can be fired on natural gas, No. 2 fuel oil, or both simultaneously.

The recirculation of flue gases into the burner flame was accomplished by passing a portion of the furnace exhaust's flue gases by means of a blower through a stainless steel air-to-air heat exchanger and combining this flow with the combustion air flow. The temperature of the recycled flue gases was maintained at ~533K (500°F) by adjusting the flow of cooling air through the heat exchanger. Good mixing of the combustion air and flue gases was assured by employing a diffuser between the combustion air/flue gas plenum and the burner.

401

A 20-cm (8-inch) diameter orifice was added to the furnace exhaust stack to stop ambient air entrainment in the exiting flue gases, resulting in inaccurate flue gas O_2 readings, and place the furnace and the flue gas recirculation (FGR) ductwork under positive pressure to reduce the infiltration of ambient air through the heat exchanger and blower.

All gas flows (combustion air, FGR, steam, atomizing air, and natural gas) were measured with the aid of orifices and manometers and are considered to be accurate to within 5%. All liquid flows (No. 2 fuel oil and water) were measured with rotameters which had been calibrated with the fluid to be measured. The installation of an O_2 analyzer in the FGR ductwork just upstream of the combustion air plenum became necessary to determine the degree of flue gas dilution with infiltrating ambient air.

Water was injected into the flame zone only when firing natural gas, and steam was injected only when firing No. 2 oil. During natural gas firing, water was injected through the unused oil port. During oil firing, steam was injected through an unused gas annulus. Temperature measurements of all flows, including the flue gas temperature, were made using type "K" (61K to 1589K) thermocouples. Flame temperature profiles were obtained using a type "R" (256K to 2033K) aspirated thermocouple. Flame temperature profile measurements were made for each of the modified conditions as well as for baseline conditions firing both natural gas and No. 2 oil.

SECTION 3

COMBUSTION MODIFICATIONS

The overall results of the combustion modification tests are most encouraging from the standpoint of NO emission reduction potential. The maximum NO reductions obtained for each modification are summarized in Table II. The average baseline NO_x emission for a steel furnace burner firing natural gas and No. 2 oil is given in Table III.

Gaseous emissions were measured at baseline conditions and at various excess air settings at full capacity and half capacity (nominally). In addition to excess air variation, steam injection and water injection were tried at full capacity firing No. 2 oil and natural gas, respectively, to reduce NO_x emissions. Flue gas recirculation was also tested firing each of the two fuels.

Figures 2 and 3 show the effect of excess oxygen on NO emissions when firing natural gas and No. 2 oil. For both fuels, NO emission peaked at about 2% O_2. As the O_2 was increased beyond 2%, the NO concentration tended to decrease. The NO concentration also decreased at excess O_2 levels below 2%, but the trend was less pronounced. (The high furnace temperatures which occurred at low excess O_2 conditions on several occasions caused NO emission at these conditions to be higher than it would have been if the temperatures had been held constant.)

There is an apparent considerable spread in the data for NO emission versus stack excess oxygen. Figures 2 and 3 suggest a family of curves for NO vs. O_2. This indicates that another important factor is involved in determining NO levels. It is believed that this factor is combustion air humidity, and that each curve in the "family" of curves represents a constant combustion air moisture content. Unfortunately, precise moisture data were unavailable at the test site. Dry bulb and relative humidity data were obtained from a weather station approximately ten miles from the test site. These data were used in the construction of Figures 4 and 5. In these figures the moisture in the combustion air was added to the H_2O injected through the burner.

Figures 4 and 5 reveal the sensitivity of NO to change in H_2O injection rate, particularly when firing No. 2 oil. The maximum percent NO reduction obtained by injecting water with natural gas was 47% as compared with 89% reduction of NO obtained by injecting steam with No. 2 oil. It was not practical to try steam injection with natural gas or water injection with No. 2 oil with this particular burner design.

Flue gas recirculation resulted in large NO reductions for both natural gas and No. 2 oil fuels (see Figures 6 and 7). The greatest decrease in NO using the FGR technique was observed when firing natural gas (88% reduction).

SECTION 4

COST ANALYSIS OF COMBUSTION MODIFICATIONS

INITIAL CAPITAL COSTS

Capital Costs of Steam and Water Injection for Steel Furnaces

For a plant which has steam generating capability but no steam piping to the furnace to which the steam injection modification is to be applied, the capital costs have been determined previously by KVB for process heater applications. For three heater sizes these costs are shown below in 1980 dollars:

2.9 MW (10×10^6 Btu/hr)	73.3 MW (250×10^6 Btu/hr)	147 MW (500×10^6 Btu/hr)
\$3,500	\$19,000	\$32,000

Although these costs were developed for a process heater modification it is not expected that they will differ substantially for a steel furnace modification. They involve only straightforward piping changes to get the steam from existing headers to the furnace itself.

Flue Gas Recirculation Capital Costs for Steel Furnaces

The capital costs determined for flue gas recirculation systems for process heaters are used here to estimate the cost of an FGR system for steel furnaces. There are only two substantial differences between an FGR system for a refinery process heater and a steel furnace system:

1. A heat exchanger may be needed in a steel furnace application in order to cool the flue gases to a temperature which can be sent through the recirculating fan. This heat exchanger could

act as a regenerator, increasing the efficiency of the unit and offsetting its cost at least in part.

2. A burner plenum would not be required in a forced-draft steel furnace, whereas it was required in a natural draft process heater for which there was not existing forced air injection capability.

The initial installed costs of a 20% FGR system are shown in Table IV in 1980 dollars.

ANNUAL OPERATING COSTS

Annual Operating Costs for Steam and Water Injection in Steel Furnaces

The total annual costs of the steam and water injection modifications, including water cost, steam generation cost, additional fuel requirement cost due to efficiency loss (calculated in the Appendix), and maintenance, are shown in Table V for three heater sizes using a 0.005 Kg/s/burner (40 lb/hr/burner) injection rate. One observes that the annual operating costs of steam and water injection are, for all practical purposes, equal. Thus, the average of the total annual costs of steam and water injection is used here for costing both modifications.

The costs of water and steam, shown in Table V, include water supply and treatment costs as well as steam generation costs (in the case of steam injection). As shown in Table V these costs are small in comparison to the cost of additional fuel input required by each modification.

Additional annual costs in the form of increased fuel requirements brought about by steam and water injection must also be considered. The additional fuel requirement is calculated in Appendix A for a subscale steel furnace with a maximum firing rate of 0.59 MW (2×10^6 Btu/hr) and 0.005 Kg/s (40 lb/hr) steam injection. The additional heat required is directly proportional to the steam or water flow rate. The relationship is given below:

$$\Delta h_s = NC_{STM}\ \dot{m}_{STM}$$

$$\Delta h_w = NC_{WATER}\ \dot{m}_{WATER}$$

Where C_{WATER} = 2387 Btu/lb and C_{STM} = 1275 Btu/lb, N is the number of burners in the furnace, and Δh is the incremental heat input requirement in units of Btu/hr. The cost increase on an annual basis may be determined, assuming an 80% use factor, as follows:

$$\text{Increase in Total Annual Fuel Cost} = \Delta h \times \frac{\text{Cost}}{\text{Unit Heat Input}} \times 8760\ \frac{h}{y} \times 0.80$$

The cost per unit heat input for typical natural gas fuel is \$2.20/10^6 Btu (1), the cost for No. 2 oil is \$4.55/10^6 Btu, and the cost of No. 6 oil is \$3.90/10^6 Btu (2). The calculation of Δh is explained in Appendix A. In Figures 8 and 9 the annual costs of steam and water injection when firing natural gas or No. 2 oil are given as a function of H_2O flow rate per burner.

FGR Annual Operating Costs

The electrical cost of fan operation, the incremental fuel costs, and maintenance costs are the chief components of the annual operating costs of a flue gas recirculation system. In the special case of steel furnaces, heat exchanger maintenance costs would be added to those used in other applications such as process heaters since the flue gases used would be much hotter (1366K or 2000°F). The annual maintenance costs are estimated to be ~10% of initial fixed capital costs.

The additional fuel costs resulting from the use of FGR are determined for 20% FGR and 2% excess O_2 in the stack. We emphasize that efficiencies calculated here assume that the flue gas temperature change from combustion zone to reinjection point is all due to heat loss to the external environment; i.e., there is no regenerative capability of the FGR system.

The additional fuel costs are directly proportional to the mass flow rate of the recirculated flue gas. The relationship used to calculate those costs is the following:

$$\Delta\ \text{Cost} = \Delta h_{FGR} \times 8760 \times 0.8 \times \frac{\text{Cost}}{\text{Unit Heat Input}}$$

Δh_{FGR} is calculated in Appendix A for these typical test conditions: flue gas temperature of 558K (546°F), flue gas density of 0.673 Kg/m^3 (0.042 lbm/ft^3), and specific heat of 1.089 kJ/kg-°C (0.26 Btu/lbm-°F).

The cost of electricity to operate the FGR fan has been estimated from data obtained by KVB. The total annual costs (not annualized) taking into account the cost of additional fuel requirements, fan electrical costs, and maintenance cost are given in Table VI for three furnace sizes for natural gas or No. 2 oil firing.

Again, it is emphasized that the incremental fuel costs shown here were determined for the worst case in which nearly all of the sensible heat of the recirculated flue gas is lost to the furnace surroundings. This situation would probably not prevail in a practical, full-size steel furnace. However, it is impossible to predict, with the data available at this time, how much heat may be retained in the furnace.

TOTAL ANNUALIZED COSTS

The initial fixed capital costs of combustion modifications are annualized making the following assumptions:

1. Straight-line depreciation of capital assets over a 12-year life span.
2. After-tax rate of return of 15%.
3. State and federal property taxes totalling 11% of the initial capital cost.
4. Insurance charges of 0.5% of the initial capital cost.
5. Debt/equity ratio of 0 (100% equity) for financing of initial fixed capital costs.
6. Annual income tax rate (state and federal) of 50%.
7. Investment tax credit of 10% (applies only to the first year of operation).

The annualized capital costs must then be added to the annual operating costs to give the total annualized cost of combustion modifications.

Total Annualized Costs of Water or Steam Injection

The calculation of total annual expenses and total annualized cost of the water or the steam injection modifications to a steel furnace are shown in Tables VII and VIII for No. 2 oil firing and natural gas firing.

The cost effectiveness of a combustion modification is defined as the total annualized cost of the modification divided by the annual NO_x emission reduction potential of the modification (in thousands of Kg). The annual NO_x emission reduction potentials for steam and water injection and for flue gas recirculation firing No. 2 oil and natural gas are given in Table IX. The cost effectiveness of steel furnace combustion modifications for two different fuels and three furnace sizes are given in Table X.

The annual fuel cost turns out to be the most significant item in the cost effectiveness calculation for steel furnaces. These costs were calculated for steel furnaces based on the annual incremental fuel requirements of combustion modifications. Certain assumptions were made in the calculation of those fuel requirements. They are explained along with those calculations in Appendix A.

SECTION 5

CONCLUSIONS

The results of the tests at the subscale steel furnace are summarized below:

1. Large NO emission reductions were obtained when firing natural gas and No. 2 oil by the method of H_2O injection and by the flue gas recirculation technique.

2. Excess air variations did not affect NO emissions significantly except at a high O_2 level, which is a less efficient mode of operation.

3. From the standpoint of NO reduction capability, without regard to efficiency considerations, the steam injection technique appeared to give the best results when firing No. 2 oil, and FGR gave the best results when firing natural gas.

4. Final calculations of the relative cost of combustion modifications indicate that steam or water injection offers the best NO removal capability for the least cost.

REFERENCES

1. American Gas Association Quarterly Report of Gas Industry Operations, American Gas Association, Second Quarter, 1979.

2. Energy User News, October 22, 1979, p. 15.

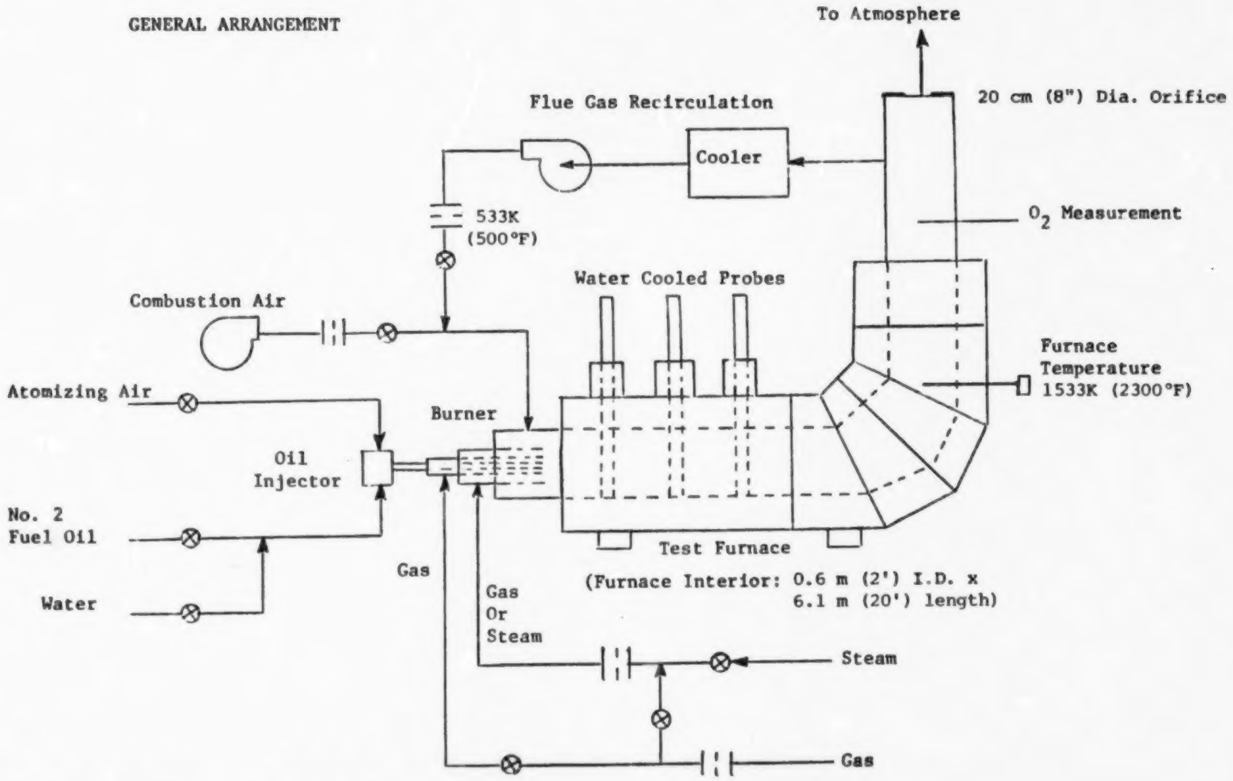

GENERAL ARRANGEMENT
To Atmosphere
20 cm (8") Dia. Orifice
Flue Gas Recirculation
Cooler
533K
(500°F)
O2 Measurement
Water Cooled Probes
Combustion Air
Furnace
Temperature
1533K (2300°F)
Atomizing Air
Burner
Oil
Injector
No. 2
Fuel Oil
Test Furnace
(Furnace Interior: 0.6 m (2') I.D. x
6.1 m (20') length)
Gas
Gas
Or
Steam
Water
Steam
Gas

Figure 1. Subscale steel furnace test schematic.

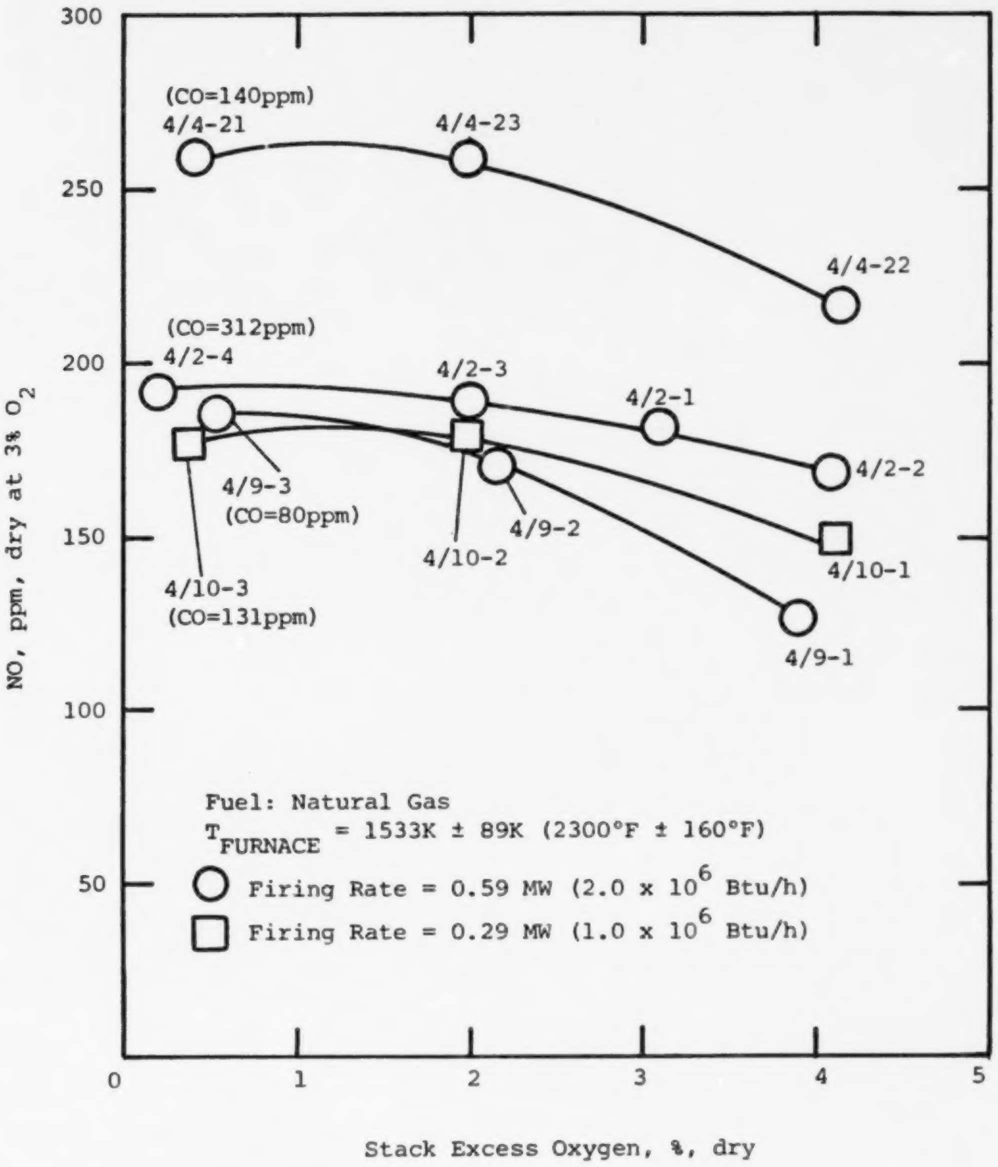


Figure 2. NO emission as a function of stack excess oxygen for a subscale steel furnace firing natural gas.

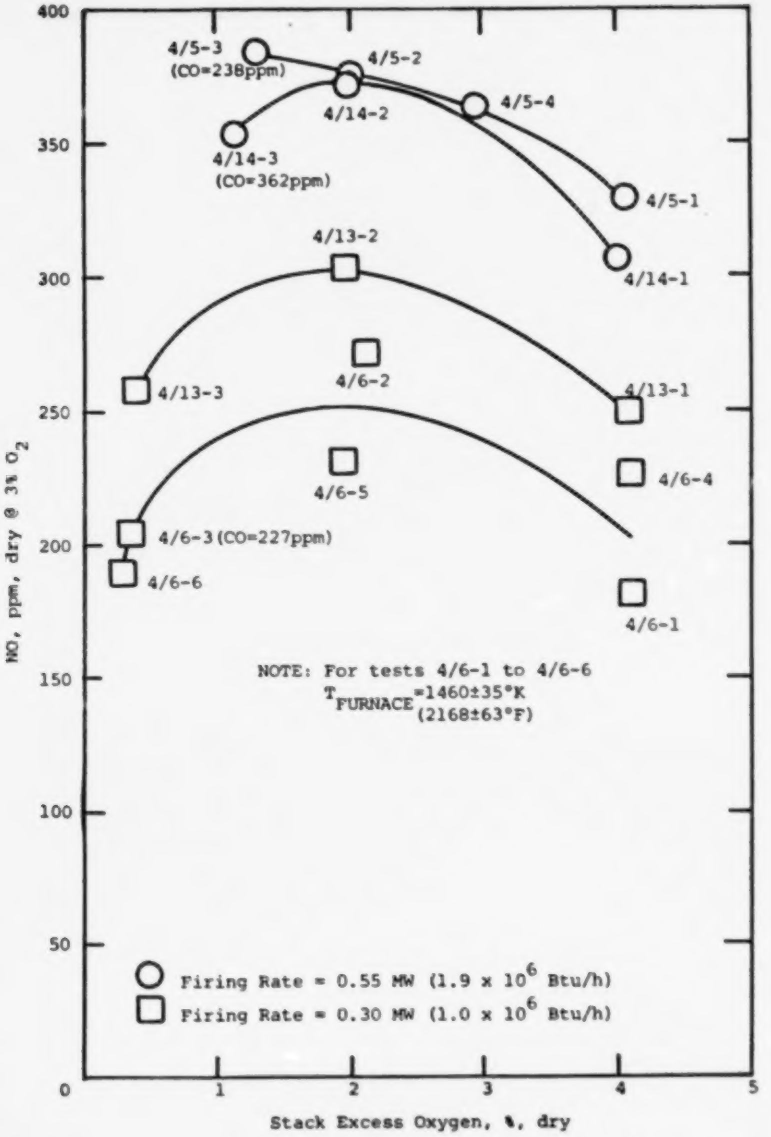


Figure 3. NO emission as a function of stack excess oxygen for a subscale steel furnace firing No. 2 oil.

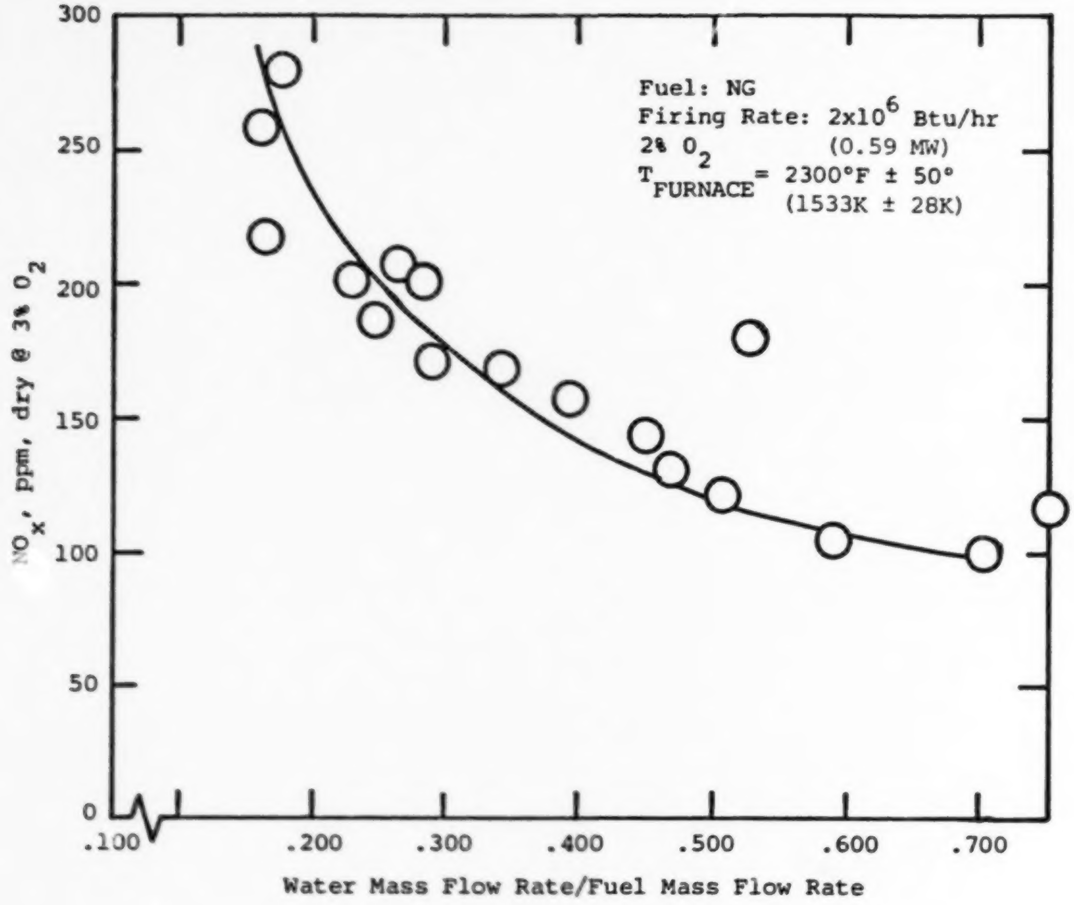


Figure 4. NO emission as a function of water injection rate for a subscale steel furnace firing natural gas.

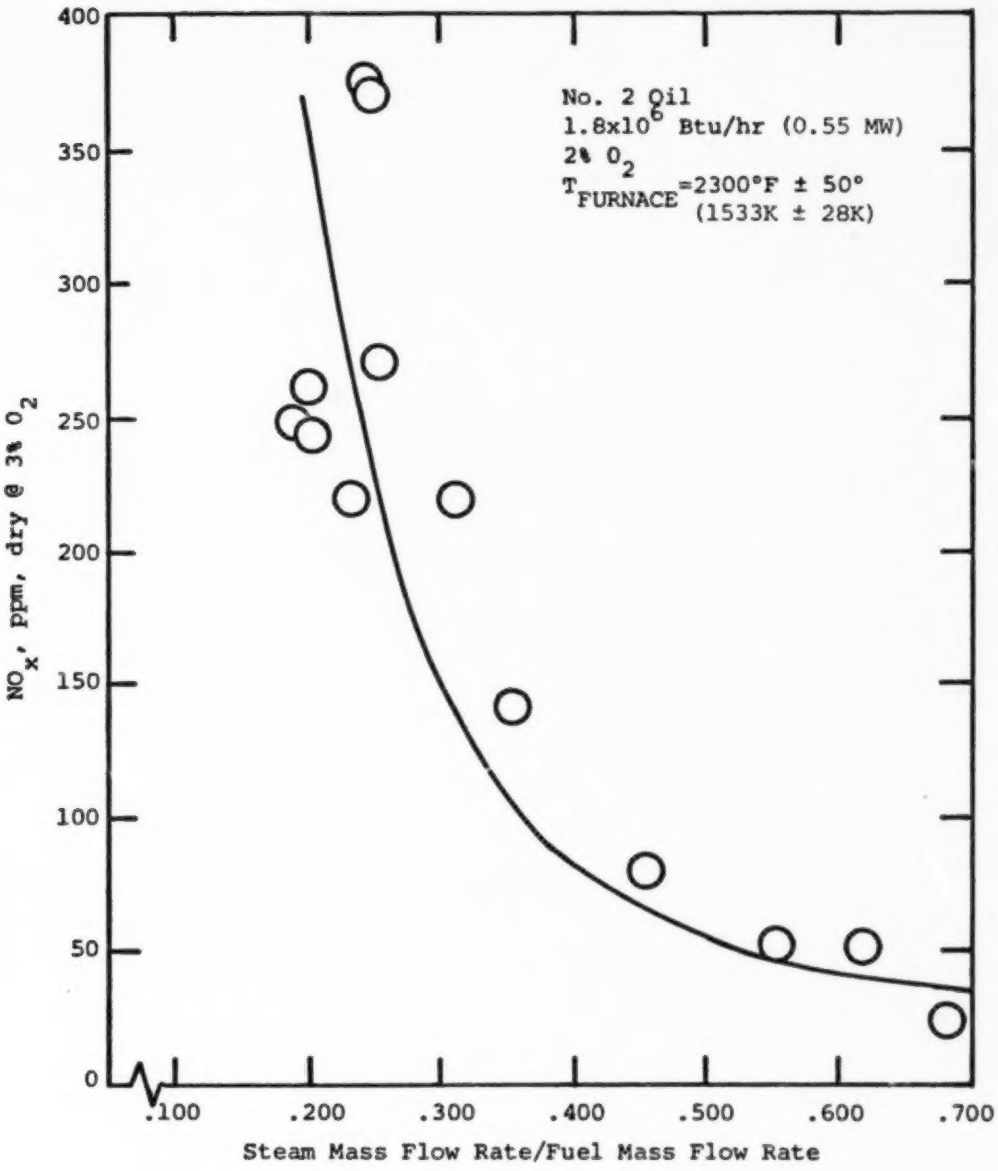


Figure 5. NO emission as function of steam injection rate for a subscale steel furnace firing No. 2 oil.

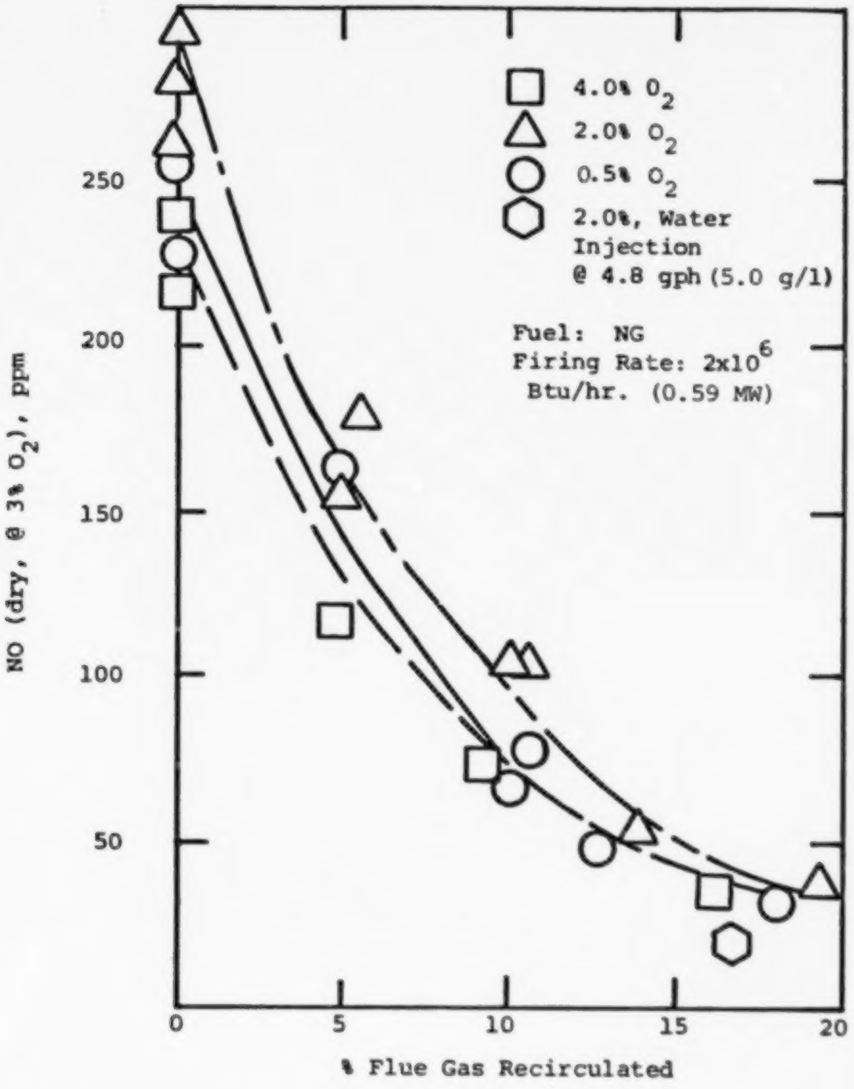


Figure 6. NO emission as a function of percent flue gas recirculated for a subscale steel furnace firing natural gas.

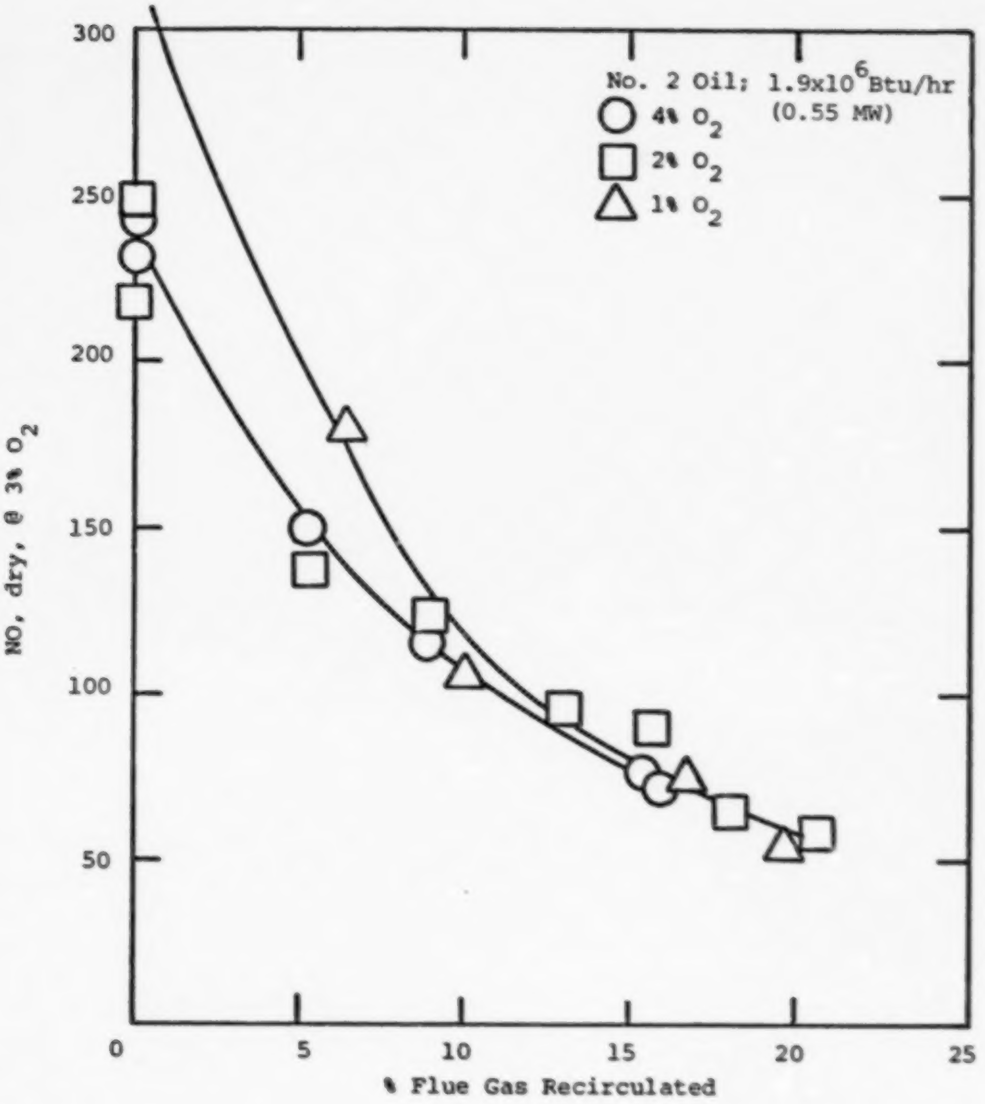


Figure 7. NO emission as a function of percent flue gas recirculated for a subscale steel furnace firing No. 2 oil.

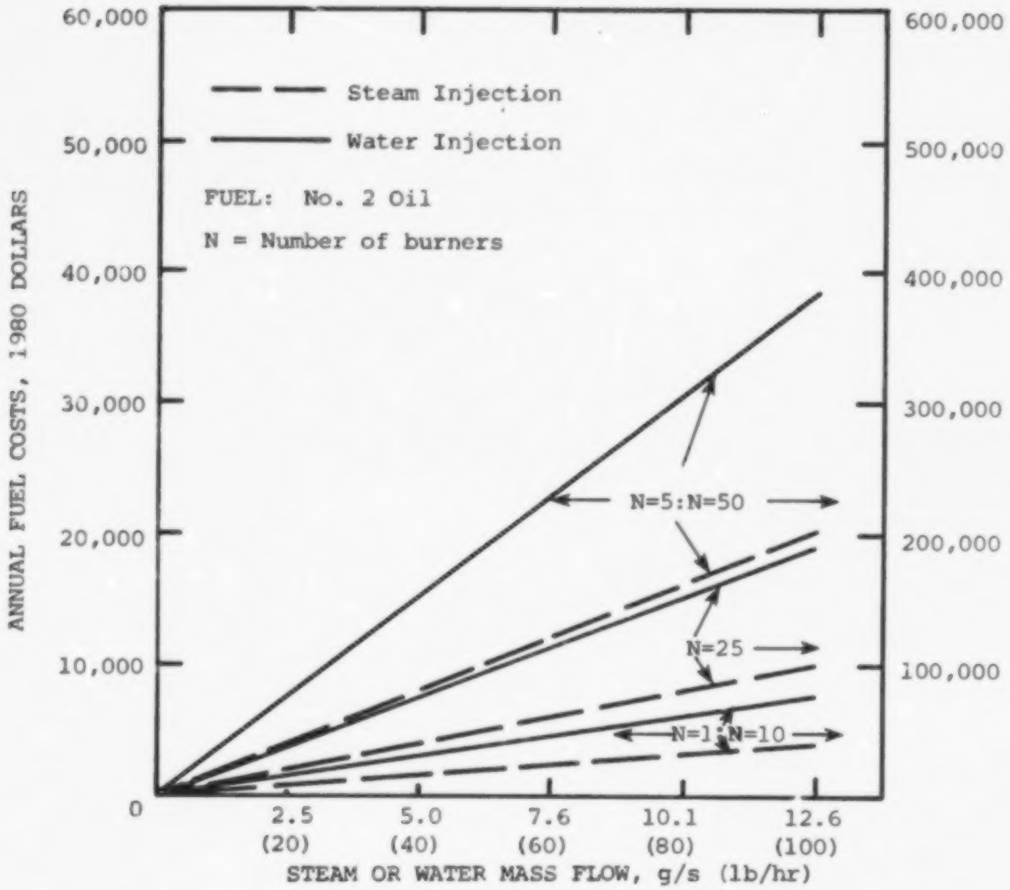


Figure 8. Annual additional fuel requirement cost with steam or water in a steel furnace firing No. 2 oil.

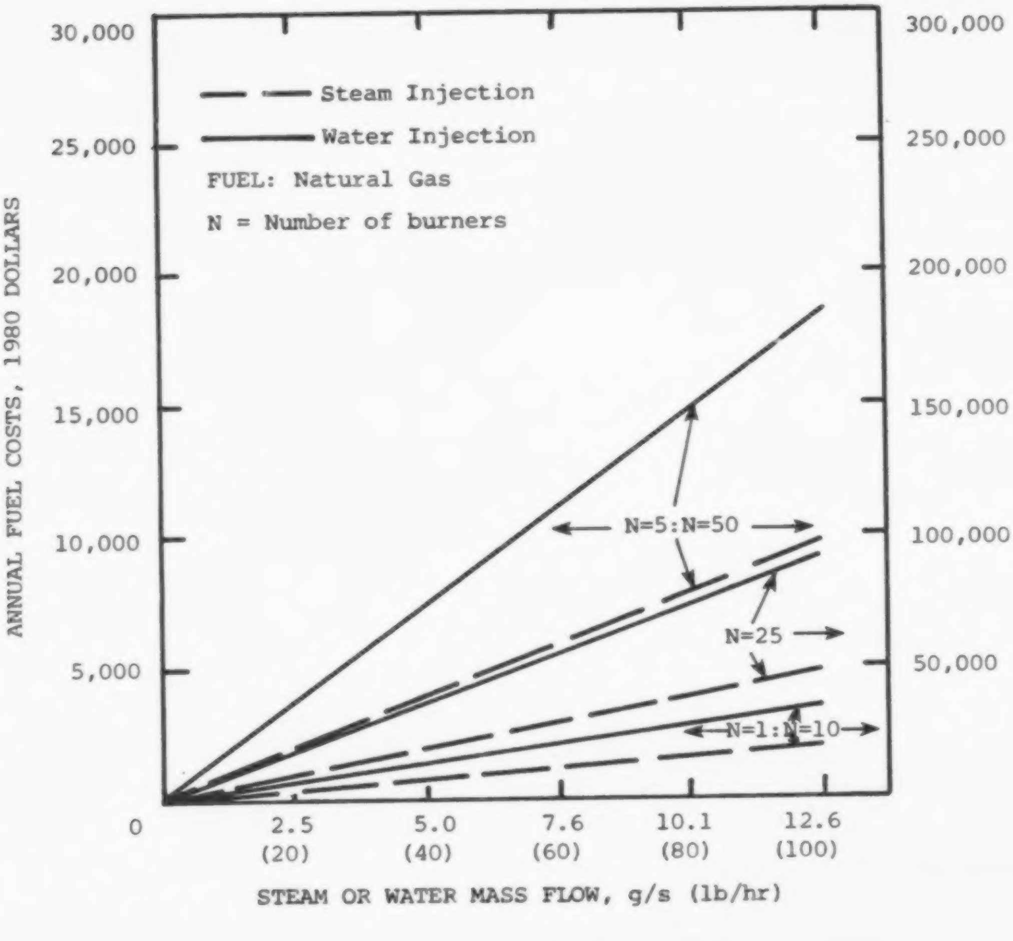


Figure 9. Annual additional fuel requirement cost with steam or water injection in a steel furnace firing natural gas.

TABLE I. EMISSION MEASUREMENT INSTRUMENTATION

Species	Manufacturer	Measurement Method	Model No.
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron Co.	Chemiluminescent	10A
Sulfur Dioxide	DuPont Instruments	UV Spectrometer	400
Smoke Spot	Bacharach	ASTM D2156-65	21-7006

TABLE II

SUMMARY OF SIGNIFICANT TEST RESULTS, SUBSCALE STEEL FURNACE BURNER

Test Number	Fuel	Combustion Modification	Firing Rate (% Cap.)	O_2 %	NO (ppm)*	% Reduction in NO From Nearest Baseline
4/3-11	NG	Water Injection	100	2.2	98	47
4/4-13	NG	FGR	100	2.0	38	88
4/3-12	NG	FGR + Water Inj.	100	1.8	24	87
4/7-2	No.2	Steam Injection	100	2.1	24	89
4/8-10	No.2	FGR	100	2.0	57	77

*NO corrected to 3% O_2, dry

TABLE III. AVERAGE BASELINE NO_x EMISSION, SUBSCALE STEEL FURNACE BURNER

(Including All Baseline Tests at Location 4)

Fuel	NO_x ppm*	NO_x ng/J	Number of Tests	Coefficient of Variation[†]
NG	222	114.6	11	0.19
No. 2	277	153.4	8	0.23

*ppm corrected to 3% O_2, dry

†Coefficient of variation = $\frac{\text{Std. deviation}}{\text{Mean}}$

TABLE IV. INITIAL INSTALLED COSTS (IN $) OF FLUE GAS RECIRCULATION

Item/Heater Size	2.9 MW ($10x10^6$ Btu/h)	73.3 MW ($250x10^6$ Btu/h)	147 MW ($500x10^6$ Btu/h)
Fan, Motor & Drive	2,000	10,000	23,000
Damper	500	500	1,000
Ductwork & Heat Exchanger	2,000	10,000	20,000
Duct Insulation	2,000	8,500	15,000
Instrumentation & Control Systems	10,000	15,000	15,000
Engineering/Design	2,000	10,000	20,000
Totals	$18,500	$54,000	$94,000

TABLE V. TOTAL ANNUAL COSTS OF STEAM AND WATER INJECTION

Costs	2.9 MW ($10x10^6$ Btu/hr)		73.3 MW ($250x10^6$ Btu/hr)		147 MW (500×10^6 Btu/hr)	
	No. 2 Oil	NG	No. 2 Oil	NG	No. 2 Oil	NG
Water	$ 22	$ 22	$ 600	$ 600	$ 1,100	$ 1,100
Additional Fuel	3,000	1,400	75,000	37,000	155,000	73,000
Total	$3,022	$1,422	$81,000	$37,600	$156,100	$84,000
Steam	$1,700	$1,000	$41,000	$21,000	$ 83,000	$43,000
Additional Fuel	1,500	750	40,000	20,000	80,000	39,000
Total	$3,200	$1,750	$81,000	$41,000	$163,000	$82,000
Average	$3,100	$1,600	$81,000	$39,300	$159,500	$83,000

TABLE VI. ANNUAL OPERATING COSTS OF 20 PERCENT FLUE GAS RECIRCULATION FOR A STEEL FURNACE FIRING NATURAL GAS OR NO. 2 OIL (1980 DOLLARS)
FLUE GAS TEMPERATURE = 533K (500°F)

Costs	2.9 MW (10×10^6 Btu/hr)	733 MW (250×10^6 Btu/hr)	147 MW (500×10^6 Btu/hr)
Additional Fuel (NG/No.2)	17,100/35,380	428,000/885,000	856,000/1,770,000
Fan Electricity	400	3,600	7,700
Maintenance	1,850	5,400	9,400
TOTAL (NG/No. 2)	19,350/37,630	437,000/894,000	873,100/1,787,100

TABLE VII. TOTAL ANNUALIZED COSTS OF WATER OR STEAM INJECTION

Annual Operating Cost (No. 2/Natural Gas)	\$3,100/1,600	\$81,000/39,300	\$159,500/83,000
State and Federal Taxes (11% of IFC)	385	2,090	3,520
Insurance (0.5% of IFC)	18	95	160
Depreciation (Straight Line over 12 years)	290	1,585	2,667
Total Annual Expenses (No. 2)	\$3,793	\$84,770	\$165,847
Total Annual Expenses (Natural Gas)	\$2,293	\$43,070	\$ 89,347
INITIAL FIXED COSTS (IFC)	3,500	19,000	32,000
(WATER OR STEAM) ROR=i=15%,n=12 Capital Recovery Factor=.1845=CR Annual Income Tax Rate=50% Investment Tax Credit=10%=i_c (1st year only)		SEE TABLE VII (REV.) ON PAGE 438	
Total Annual Capital Factor* (ACF)=.2773			
Annual Capital Charge (=IFCxACF)	971	5,269	8,875
TOTAL ANNUALIZED COSTS (1980 DOLLARS)			
No. 2 Oil	4,764	90,039	174,722
Natural Gas	3,264	48,339	98,222

*ACF = $CR + T\left(CR - \frac{1}{n}\right) - \frac{i_c}{n}$

where CR = capital recovery factor = $\frac{i}{1-(1+i)^{-n}}$

and T = 1.0 (for debt/equity ratio of 0)

TABLE VIII. TOTAL ANNUALIZED COSTS OF FGR

Annual Operating Costs (No. 2/NG) =	37,630/19,350	894,000/437,000	1,787,100/873,100
State and Federal Taxes (11% of IFC)	2,035	5,940	10,340
Insurance (0.5% of IFC)	100	270	470
Depreciation (Straight Line over 12 Years)	1,540	4,500	7,830
TOTAL ANNUAL EXPENSES (No. 2)	41,305	904,710	2,678,840
TOTAL ANNUAL EXPENSES (NG)	23,025	447,710	891,740
INITIAL FIXED COSTS	18,500	54,000	94,000
(ROR =i=15%,n=12			
Capital Recovery Factor=.1845	SEE	TABLE VIII (REV.)	ON PAGE 439
Annual Income Tax Rate=t=50%			
Investment Tax credit=i_c=10% (1st year only)			
Total Annual Capital Factor =.2773			
Annual Capital Charge	5,131	14,976	26,069
TOTAL ANNUALIZED COSTS (1980 DOLLARS)			
No. 2	46,436	919,686	2,704,909
NG	28,156	462,686	917,809

TABLE IX. BASELINE NO_x EMISSIONS FROM A STEEL FURNACE

Modification	Fuel	Heat Input MW	NO Concentration ng/J	Annual Emission 10^3Kg NO	Reduction Percent	Annual Reduction 10^3 Kg NO
Steam	No.2	2.93	153.4	11.3	89	10.1
Steam	No.2	73.2	153.4	283	89	252
Steam	No.2	147	153.4	568	89	506
Water	NG	2.93	114.6	8.5	47	4.0
Water	NG	73.2	114.6	211	47	99
Water	NG	147	114.6	425	47	200
FGR	No.2	2.93	153.4	11.3	77	8.7
FGR	No.2	73.2	153.4	283	77	218
FGR	No.2	147	153.4	568	77	437
FGR	NG	2.93	114.6	8.5	88	7.5
FGR	NG	73.2	114.6	211	88	186
FGR	NG	147	114.6	425	88	374

$$\text{Annual } NO_x \text{ Emission} \equiv \frac{10^3 \text{ Kg NO}}{y} = 0.0252 \times \text{MW} \times \frac{ng}{J}$$

TABLE X. COST EFFECTIVENESS OF COMBUSTION MODIFICATIONS ON A STEEL FURNACE ($\$/10^3$ Kg OF NO_x REDUCTION) INCLUDING ANNUAL INCREMENTAL FUEL COSTS

Modification	Furnace Heat Input 2.9 MW ($10x10^6$ Btu/hr)	73.3 MW ($250x10^6$ Btu/hr)	147 MW ($500x10^6$ Btu/hr)
STEAM INJECTION			
No. 2 Oil	472	357	345
NG	323	192	194
WATER INJECTION			
No. 2 Oil	1,191	909	874
NG	816	488	491
FLUE GAS RECIRCULATION			
No. 2 Oil	5,337	4,219	6,190
NG	3,754	2,488	2,454

SEE TABLE X (REV.) ON PAGE 440

APPENDIX A

CALCULATION OF INCREMENTAL FUEL REQUIREMENTS OF COMBUSTION MODIFICATIONS TO A STEEL FURNACE

The calculation of the incremental heat requirement of steam or water injection or flue gas recirculation when applied to a steel furnace necessitates the assumption that these modifications have no effect on furnace thermal efficiency other than the additional thermal losses caused by having to heat the injected materials to combustion temperatures. Thus, the effects of the combustion modifications on convective or radiative heat transfer rates, which also affect furnace efficiency, are not considered in this report.

In an actual application, the convective heat transfer rates from the combustion gases to the steel itself will probably increase because of the higher mass flow of gases through the furnace brought about by the injection of additional material. This may partially offset the efficiency degradation associated with the added thermal load of the injected material.

In addition, the radiative heat transfer rate may also be increased by flue gas recirculation or by steam or water injection. The increase in the partial pressure of CO_2 and H_2O resulting from the injection of these materials would tend to increase the emissivity of the combustion gases and, therefore, the radiative heat transfer rate to the steel.

The effects of altered convection and radiative heat transfer need to be studied further in order to develop more meaningful efficiency assessments of the combustion modifications discussed in this section.

The incremental heat requirements for steel furnace combustion modifications are calculated in the order of increasing complexity, beginning with steam injection, followed by water injection and, finally, flue gas recirculation. The percent increase in heat load is assumed equal to the percent increase in fuel required.

The incremental heat requirement per burner of steam injection at 5.0 g/s (40 lb/hr) injected steam flow rate is defined as follows:

Δh_{STM} = heat required to take steam from the injection conditions to the furnace bulk gas temperature, T_F

$$= \dot{m}_{STM} \, (h_F - h_{IN})$$

For P_{IN} = 1 atm, T_{IN}=273K, P_F=1 atm, and T_F=1755K (typical measured operating temperature)

h_f = 3384 kJ/kg (1,455 Btu/lb) and

h_{IN} = 419 kJ/kg (180 Btu/lb)

Thus,

Δh_{STM} = 0.015 MW (51,000 Btu/hr)

= 2.56% of experimental burner capacity of 0.586 MW (2×10^6 Btu/hr)

The incremental heat requirement per burner for 5.0 g/s (40 lb/hr) injected water flow rate is determined below. This requirement includes the heat necessary to raise the water temperature to the boiling point, complete the phase change to steam, and heat the steam to the furnace bulk gas temperature.

$$\Delta h_{WATER} = \Delta h_{STM} + \dot{m}_{H_2O} \left[\Delta h_{fg} + Cp_{H_2O(\ell)} \, (T_{B.P.} - T_{IN}) \right]$$

Where

Δh_{fg} = heat of vaporization of water at p = 1 atm,

T = 373K (212°F) = 2256 kJ/kg (970 Btu/lb)

$Cp_{H_2O(\ell)}$ = specific heat of water

$T_{B.P.}$ = 373K (212°F) = boiling point of water at p=1 atm

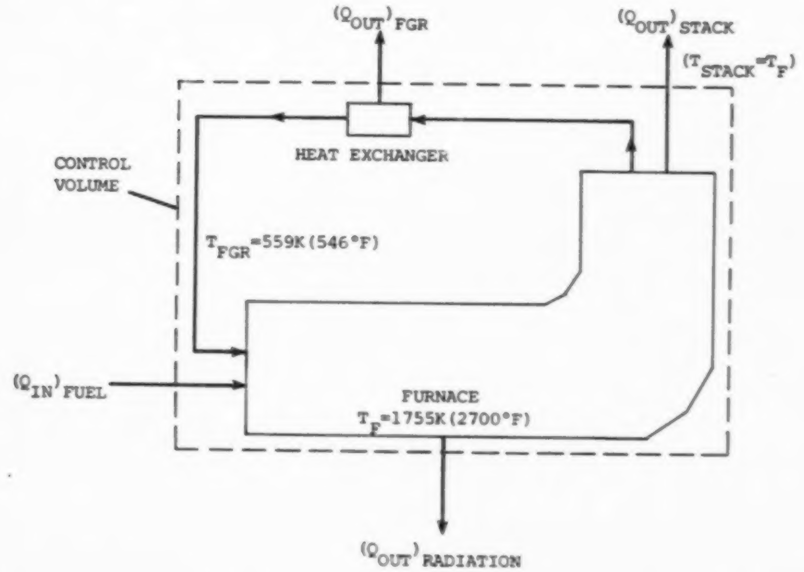
T_{IN} = injected water temperature

For T_{IN} = 294K (70°F),

Δh_{WATER} = 0.028 MW (95,480 Btu/hr)

= 4.75% of experimental burner capacity.

The heat losses associated with flue gas recirculation in a steel furnace arise from the cooling of the flue gas temperature to the reinjection temperature. In the experimental arrangement most of this cooling occurred in an air-gas heat exchanger, and no heat was recovered; i.e., all of the heat was lost to the ambient air. It is emphasized here that in a practical application of flue gas recirculation much of this heat could be retained within the furnace proper by combustion air preheat or some other means of waste heat recovery. The following diagram illustrates the calculation of furnace efficiency for the steel furnace.


$(Q_{OUT})_{FGR}$
$(Q_{OUT})_{STACK}$
$(T_{STACK}=T_F)$
HEAT EXCHANGER
CONTROL VOLUME
T_{FGR}=559K (546°F)
$(Q_{IN})_{FUEL}$
FURNACE
T_F=1755K (2700°F)
$(Q_{OUT})_{RADIATION}$

One observes from this drawing the increased heat loss from the steel furnace with FGR as compared to a furnace without FGR. In the calculations which follow we assume that there are no factors influencing furnace efficiency other than this heat loss. This assumption may not be strictly valid, however, for two reasons:

1. The convective heat transfer coefficient of the combustion gases in the furnace should increase with the increased mass flow through the furnace due to FGR, thereby increasing the convective heat transfer to the steel.

2. The recirculation of flue gases containing large amounts of the radiative species CO_2 and H_2O may increase the emissivity of the combustion gases within the furnace, thus increasing radiative heat transfer rates to the steel. (This is also especially true for the case of H_2O injection where the volume fraction of H_2O in the combustion gases is significantly increased.)

The incremental heat (fuel) requirement for 20% FGR is determined below:

$$\Delta h_{FGR} = \dot{m}_{FGR}(Cp)_{FGR}(T_F - T_{FGR})$$

where $(Cp)_{FGR}$ = specific heat of the flue gas

T_{FGR} = flue gas temperature at point of injection into the furnace

$\dot{m}_{FGR}$ = recirculated flue gas mass flow rate

For Test #4/4-13,

T_F = 1755K (2700°F), T_{FGR} = 559K (546°F)

$(C_p)_{FGR}$ = 1.09 kJ/Kg-K (0.26 Btu/lbm-°R),

and $\dot{m}_{FGR}$ = 0.051 kg/s (400.8 lbm/hr)

and so

Δh_{FGR} = 0.066 MW (224,464 Btu/hr)

= 11.2% of burner heat input capacity

Thus, with no waste heat recovery, and neglecting the effects of the combustion modifications on convective and radiative heat transfer, the additional fuel requirements are summarized in Table A-1.

TABLE A-1. INCREMENTAL FUEL REQUIREMENTS OF COMBUSTION MODIFICATIONS TO A STEEL FURNACE

Modification	Percent Increase In Fuel Consumption
Steam Injection	2.56
Water Injection	4.75
Flue Gas Recirculation	11.20

ADDENDUM

SUBSCALE TESTS OF COMBUSTION MODIFICATION FOR STEEL FURNACES

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COST CALCULATIONS FOR FLUE GAS RECIRCULATION APPLIED TO STEEL FURNACES - CASE II

If one may assume complete recovery of the flue gas energy in the recirculated flue gas such that the only losses in the steel furnace system are the stack losses, then there will be no fuel penalty associated with the FGR modification. In this instance, the annual operating costs of 20 percent FGR in a steel furnace will consist of only the fan electrical and system maintenance cost elements. The annual operating costs for three heater sizes assuming full recovery of the heat of the recirculated flue gas is shown in Table I.

TABLE I. ANNUAL OPERATING COSTS FOR A STEEL FURNACE HAVING 20 PERCENT FGR (1980 $)

Heater Size	2.9 MW	73.3 MW	147 MW
Fan Electricity	$ 400	$3,600	$7,700
Maintenance	1,850	5,400	9,400
Total	$2,250	$9,000	$17,100

The revised total annualized costs of FGR on steel furnaces are shown in Table II.

TABLE II. TOTAL ANNUALIZED COSTS OF 20 PERCENT FGR ON A STEEL FURNACE WITH WASTE HEAT RECOVERY (1980 $)

2.9 MW	73.3 MW	147 MW
$9,516	$30,186	$53,979

The annual NO_x reduction capability of the FGR modification and the cost effectiveness (equal to the total annualized cost divided by the annual NO_x reduction) are given in Table III.

TABLE III. ANNUAL NO_x EMISSION REDUCTION AND COST EFFECTIVENESS OF FGR (1980 $)

	2.9 MW		73.3 MW		147 MW	
Heater Size	No. 2 Oil	NG	No. 2 Oil	NG	No. 2 Oil	NG
Annual NO_x Emission Reduction Capability (Mg/y)	8.7	7.5	218	186	437	374
Cost Effectiveness ($/Mg)	1094	1269	138	162	124	144

Note that if the assumption of total waste heat recovery from the recirculated flue gas is valid (as could be the case if the flue gas for FGR comes from the outlet of a waste heat boiler or a regenerative heat exchanger), then flue gas recirculation becomes more attractive than either the steam or water injection modifications for larger heater sizes (73.3 MW and up). For small heaters, however, it is not as cost effective as steam injection with either No. 2 oil or natural gas fuels nor is it as cost effective as water injection firing natural gas fuel.

The original Tables VII, VIII, and X in this report have been recently revised and the updated versions are shown below. The cost effectiveness of flue gas recirculation with full heat recovery may be compared to the cost effectiveness calculations in the revised Table X.

When the cost effectiveness values in Table X (Rev.) and Table III are plotted on log-log paper against heater size, one finds that for No. 2 oil fuel FGR with heat recovery capability has the lowest cost per Mg NO_x reduction for heaters larger than 13.5 MW (46 x 10^6 Btu/h). For natural gas fuel, FGR with heat recovery becomes cheaper than water injection for heater sizes greater than 8.5 MW (29 x 10^6 Btu/h) and it is cheaper than steam injection at heater sizes in excess of 60 MW (205 x 10^6 Btu/h).

TABLE VII (REV.) TOTAL ANNUALIZED COSTS OF WATER OR STEAM INJECTION

Annual Operating Cost (No. 2/Natural Gas)	\$3,100/1,600	\$81,000/39,300	\$159,500/83,000
State and Federal Taxes (11% of IFC)	385	2,090	3,520
Insurance (0.5% of IFC)	18	95	160
Total Annual Expenses (No. 2)	\$3,503	\$83,185	\$163,180
Total Annual Expenses (Natural Gas)	\$2,003	\$41,485	\$86,680
INITIAL FIXED COSTS (IFC)	3,500	19,000	32,000
(WATER OR STEAM) ROR=i=15%,n=12 Capital Recovery Factor=.1845=CR Annual Income Tax Rate=50% Investment Tax Credit=10%=i_c (1st year only)			
Total Annual Capital Factor* (ACF)=.2773			
Annual Capital Charge (=IFCxACF)	971	5,269	8,875
TOTAL ANNUALIZED COSTS (1980 DOLLARS)			
No. 2 Oil	4,474	88,454	172,055
Natural Gas	2,974	46,754	95,555

$$\text{*ACF} = CR + T\left(CR - \frac{1}{n}\right) - \frac{i_c}{n}$$

$$\text{where } CR = \text{capital recovery factor} = \frac{i}{1-(1+i)^{-n}}$$

and T = 1.0 (for debt/equity ratio of 0)

TABLE VIII (REV.) TOTAL ANNUALIZED COSTS OF FGR

Annual Operating Costs (No. 2/Natural Gas)	37,630/19,350	894,000/437,000	1,787,100/873,100
State and Federal Taxes (11% of IFC)	2,035	5,940	10,340
Insurance (0.5% of IFC)	100	270	470
Total Annual Expenses (No. 2)	$39,765	$900,210	$1,797,910
Total Annual Expenses (Natural Gas)	$21,485	$443,210	$883,910
INITIAL FIXED COSTS	18,500	54,000	94,000
ROR=i=15%,n=12			
Capital Recovery Factor=.1845			
Annual Income Tax Rate=t=50%			
Investment Tax Credit=i_c=10% (1st year only)			
Total Annual Capital Factor =.2773			
Annual Capital Charge	5,131	14,976	26,069
TOTAL ANNUALIZED COSTS (1980 DOLLARS)			
No. 2 Oil	44,896	915,186	1,823,979
Natural Gas	26,616	458,186	909,979

TABLE X (REV.) COST EFFECTIVENESS OF COMBUSTION MODIFICATIONS
ON A STEEL FURNACE ($\$/10^3$ Kg OF NO_x REDUCTION)
INCLUDING ANNUAL INCREMENTAL FUEL COSTS

Modification	Furnace Heat Input 2.9 MW (10×10^6 Btu/hr)	 73.3 MW (250×10^6 Btu/hr)	 147 MW (500×10^6 Btu/hr)
STEAM INJECTION			
No. 2 Oil	443	351	340
NG	294	186	189
WATER INJECTION			
No. 2 Oil	1,119	893	860
NG	744	472	478
FLUE GAS RECIRCULATION			
No. 2 Oil	5,160	4,198	4,174
NG	3,549	2,463	2,433